REMOTE PLASMA DEPOSITION OF TEXTURED ZINC OXIDE WITH FOCUS ON THIN FILM SOLAR CELL APPLICATIONS

MATERIAL PROPERTIES, PLASMA PROCESSES AND FILM GROWTH

PROEFSCHRIFT

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ROLAND GROENEN

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prof.dr.ir. M.C.M. van de Sanden
en
prof.dr. R.E.I. Schropp

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RESEARCH FRAMEWORK, OVERVIEW AND PROSPECTIVE
I. FRAMEWORK

A. Transparent conducting oxides

Simultaneously possessing transparency in the visible region, close to that of insulators, and electrical conductivity, close to that of metals, transparent conducting oxide (TCO) thin films form a highly attractive class of materials for a wide variety of applications like thin film solar cells, architectural glazing, flat panel displays, electro chromic devices, surface acoustic wave devices and gas sensors. Each application however sets different demands on the material properties. An appropriate measure of the performance of a transparent conducting oxide reflecting its intrinsic, i.e. bulk, quality is the ratio of the electrical conductivity $\sigma$ to the visible absorption coefficient $\alpha$. The quantity $\sigma/\alpha$ is a Figure of Merit (FM) for rating transparent conducting oxides, the larger the value of this quantity the better the performance of the transparent conducting oxide. Besides intrinsic quality, generally also specific extrinsic quality is required like, e.g., mechanical, chemical and thermal durability, surface morphology, and etchability. Deposition temperature, cost and environmental impact are other factors that may influence the choice of transparent conducting oxide for any particular application. An extensive overview of transparent conducting oxide material properties and applications is presented by Hartnagel et al.\textsuperscript{2}

B. Zinc oxide

A transparent conducting oxide of emerging technological interest is zinc oxide (ZnO). ZnO generally exhibits the hexagonal wurtzite crystal structure. In this structure, zinc atoms are positioned in a slightly deformed hexagonal close packed structure, with crystal planes stacked in an ABABA… order. Every zinc atom is located in the centre of a tetrahedron formed by four oxygen atoms with every such tetrahedron pointing in the same direction along the main crystal axis. The result is a normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy.

ZnO exhibits a direct, wide band gap (~ 3.37 eV).\textsuperscript{3} The band gap can be tuned via divalent substitution on the cation site producing heterostructures, e.g. cadmium substitution\textsuperscript{4} leads to a reduction of the band gap (~ 3.0 eV) whereas magnesium substitution\textsuperscript{5} could increase the band gap (~ 4.0 eV) while maintaining the wurtzite crystal structure. Stoichiometric zinc oxide is an insulator due to its wide band gap. Electrical conductivity is directly related to the density and mobility of charge carriers. Whereas the mobility mainly depends on the mechanism by which the carriers are scattered by lattice imperfections, e.g. ionised impurity scattering and grain boundary scattering,\textsuperscript{2} the density is determined by intrinsic (defects) or extrinsic (dopants) charge carriers present. Intrinsic n-type conductivity has been attributed to interstitial zinc, oxygen vacancies or hydrogen.\textsuperscript{6-11} The intrinsic defect levels leading to n-type conductivity lie approximately 0.01 to 0.05 eV below the conduction band. Typically, intrinsic thin film resistivities as low as $10^{2}$ to $10^{3}$ $\Omega$cm could be achieved.\textsuperscript{12} For comparison, intrinsic single crystals have typical resistivities in the range of 1 to 10 $\Omega$cm.\textsuperscript{13,14} Extrinsic n-type conductivity arises from appropriate cationic (trivalent, e.g. aluminium, indium, tin, gallium) or anionic (monovalent, e.g. bohr, chlorine, fluorine) substitution. The lowest resistivities reported are in the range of 1.2 to 2 $10^{4}$ $\Omega$cm.\textsuperscript{15-17} ZnO exhibits a strong near band gap ultraviolet photoluminescence emission attributed to an exciton state, as the exciton binding energy is in the order of ~ 60 meV.\textsuperscript{18-20} Visible photoluminescence emission has been attributed to defect states, e.g. transitions involving self activated centres formed by a double ionised zinc vacancy and zinc interstitial,\textsuperscript{21} donor
acceptor recombination involving an impurity acceptor,\textsuperscript{22} oxygen vacancies,\textsuperscript{23-26} and interstitial oxygen.\textsuperscript{27-29} A summary of the physical properties of wurtzite ZnO is displayed in Table 1.

Table 1. Physical properties of wurtzite ZnO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P6(_3)mc</td>
</tr>
<tr>
<td>Lattice parameter (a)</td>
<td>0.32475 – 0.32501 nm\textsuperscript{30-34}</td>
</tr>
<tr>
<td>Lattice parameter (c)</td>
<td>0.52042 – 0.52075 nm\textsuperscript{30-34}</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g cm(^{-3})</td>
</tr>
<tr>
<td>Sublimation point</td>
<td>2248 K</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>183 GPa\textsuperscript{35,35}</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>111.2 ± 4.7 GPa\textsuperscript{30}</td>
</tr>
<tr>
<td>Hardness</td>
<td>5.0 ± 0.1 GPa\textsuperscript{37}</td>
</tr>
<tr>
<td>Effective electron mass</td>
<td>0.28 m\textsuperscript{37}</td>
</tr>
<tr>
<td>Electron carrier concentration</td>
<td>6.0 \texttimes 10\textsuperscript{16} cm(^{-3})</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>205 cm(^2) V(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV\textsuperscript{18-20}</td>
</tr>
</tbody>
</table>

\textsuperscript{3} Bulk ZnO single crystal grown by vapour phase transport method.

ZnO films have been deposited by numerous techniques including molecular beam epitaxy,\textsuperscript{39,40} pulsed laser deposition,\textsuperscript{41-43} atomic layer deposition,\textsuperscript{44} (magnetron) sputtering,\textsuperscript{45,46} chemical vapour deposition\textsuperscript{46,47} and spray pyrolysis.\textsuperscript{48,49} Plasma-enhanced chemical vapour deposition is utilised only on a limited scale.\textsuperscript{50,51} ZnO can be deposited from zinc acetate,\textsuperscript{52} zinc acetylacetonate,\textsuperscript{53} diallyl zinc\textsuperscript{46,47} or zinc amide\textsuperscript{54} by chemical vapour deposition. A commonly used metal organic zinc precursor is diethylzinc. Oxidation can occur by using oxygen,\textsuperscript{55,56} water,\textsuperscript{57} alcohol,\textsuperscript{58,59} nitrous oxide,\textsuperscript{60,61} carbon dioxide\textsuperscript{62} or an oxygen containing cyclic compound.\textsuperscript{61} ZnO films can also be deposited from alkylzinc alkoxides without any additional oxygen source.\textsuperscript{62}

C. Scope of the thesis

The increasing interest in ZnO challenges the development of sophisticated synthesis technologies allowing for highly tailorable material properties.\textsuperscript{63} The goal of this thesis is to design and develop a process for low temperature deposition of textured ZnO films using expanding thermal plasma (ETP). An expanding thermal plasma has been used successfully for the deposition of diamond,\textsuperscript{64} hydrogenated amorphous carbon\textsuperscript{65-71} and carbon nitride,\textsuperscript{52} hydrogenated amorphous\textsuperscript{72-74} and microcrystalline\textsuperscript{55} silicon, silicon nitride,\textsuperscript{76} and silicon oxide;\textsuperscript{77,78} high deposition rates are obtained while maintaining good material quality. The expanding thermal plasma is the ultimate remote plasma; in contrast with e.g. electron cyclotron resonance, remote microwave and inductively coupled plasmas, the downstream properties do not influence the plasma source characteristics at all due to the large pressure difference between source and reactor chamber.\textsuperscript{79} As opposed to direct plasmas, the substrate holder or electrode does not play a role in plasma production implying the absence of any significant ion bombardment\textsuperscript{80} and ultraviolet light
exposure. The remote configuration of the expanding thermal plasma technique allows separate control of plasma production, gas phase chemistry, and substrate surface treatment, e.g. deposition, etching, facilitating fundamental studies of material properties, plasma processes and film growth.

The tailoring of ZnO material properties is emphasised to raise the prospect of a wide variety of applications. The relation between material properties, plasma processes and film growth is addressed; dedicated property control requires a profound knowledge of e.g. the plasma processes, plasma composition, surface composition and (sub) surface reactions interacting.

As an example, suitability for application as a front contact in thin film solar cells is demonstrated. Here, the transparent conducting oxide is of particular importance providing the top electrode, which serves as current collector without blocking the useful sun light to be converted, see Fig. 1. In addition, the transparent conducting oxide quality of relevance for application as a front contact in thin film amorphous silicon pin solar cells includes a strong hydrogen plasma resistance and in particular an appropriate textured rough surface morphology for effective light trapping. The increase in optical path length of light inside the cell induces the requirement of less amount of device material, e.g. a less thick intrinsic layer in thin film amorphous or microcrystalline silicon solar cells for obtaining sufficient photovoltaic action. The reduction of thickness reduces the light induced degradation of the cell efficiency with respect to its initial value (Staebler-Wronski effect). A high stability in hydrogen containing atmospheres, e.g. silane plasma discharges, is of particular relevance with respect to the deposition of microcrystalline silicon for thin film solar cell applications generally requiring a high hydrogen dilution.

Fig. 1. (a) Schematic representation of a typical thin film amorphous silicon solar cell on glass. The incoming photons with sufficient energy, i.e. larger than the band gap, are absorbed in the intrinsic amorphous silicon layer creating electron-hole pairs. The electrons and holes are separated by the internal electric field generated by the p- and n-type doped layers and the charge is collected at the electrodes. (b) Cross-sectional transmission electron microscopy (TEM) micrograph representing a pin amorphous silicon solar cell on glass. The highly reflective silver back electrode acts as a back reflector.

Every chapter of this thesis is a journal publication dealing with a different aspect of the expanding thermal plasma ZnO deposition. Demonstration of low temperature textured ZnO deposition from oxygen, diethyl zinc and additionally for doped films trimethyl aluminum utilizing the expanding thermal plasma technique is presented in Chapter 1. The effect of aluminum doping is described in detail in Chapter 2 using spectroscopic ellipsometry to evaluate optical and electronic film properties. Property control of expanding
thermal plasma deposited textured ZnO is addressed in Chapter 3 particularly considering the interdependence of electrical conductivity, film composition and film morphology. Suitability for application as a front contact in thin film amorphous silicon pin solar cells is demonstrated. The relation between plasma processes, film growth and material properties is discussed in Chapter 4 employing complementary in-situ diagnostics, i.e. Langmuir probe, optical emission spectroscopy and mass spectrometry, in order to attempt elucidating the deposition mechanism and species dominantly responsible for film growth. Considering the recently recognized role of hydrogen in ZnO film modification, Chapter 5 describes the demonstration of fast dry etching using expanding thermal argon – hydrogen plasma. In-situ spectroscopic ellipsometry is applied to evaluate the process in terms of compositional and morphological film modification. In order to outline a clear overview of this thesis, here the expanding thermal plasma technique and ZnO deposition will be considered in brief.

II. REMOTE PLASMA DEPOSITION OF TEXTURED ZINC OXIDE

A. Expanding thermal plasma technique

The plasma source is a wall-stabilised cascaded arc as depicted in Fig. 2. It consists of three cathodes, a stack of circular copper plates insulated from each other by boron nitride rings and a grounded anode plate. The arc is vacuum-sealed with O-rings; the cathodes, plates, and anode are water-cooled. A subatmospheric argon plasma (0.3 – 0.4×10⁵ Pa) is generated in a current controlled dc discharge (30 – 70A); the cathode tips are made of tungsten with 2% lanthanum. The plasma in the arc is thermal with an electron density of ~10²² m⁻³ and an electron and heavy particle temperature of both ~1 eV. The plasma emanates from the cascaded arc through a nozzle, expands supersonically into a low-pressure reactor chamber (25 – 250 Pa), shocks, and flows at subsonic velocity towards a substrate. In the supersonic expansion and shock, the electron density is reduced to ~10¹⁹ m⁻³, the electron temperature to ~0.1 – 0.3 eV (Fig. 2).
the coupling between the electrons and heavy particles is weak leading to a temperature non-equilibrium during the expansion. The directed velocity at the centre of the plasma beam is estimated from e.g. Doppler-shifted Laser Induced Fluorescence (LIF) measurements to be approximately 1000 m s\(^{-1}\).\(^{18}\) The supersonic expansion, shock region, and subsonic expansion have been investigated in detail.\(^{39-42}\)

Downstream of the arc outlet, the precursor gases can be added to the plasma by means of a punctured ring. Electron-induced molecular dissociation or ionisation is unlikely to occur because of the low electron temperature;\(^{79}\) the plasma chemistry is controlled dominantly by (\(\text{Ar}^+, e^-\)) emanating from the arc. Deposition or etching can subsequently take place at a temperature-controlled substrate.

**B. Expanding thermal plasma reactor set up**

In order to demonstrate feasibility of the expanding thermal plasma technique for ZnO deposition, films are deposited on glass substrates using a commercial Aixtron AIX 2300 MX pre-production reactor set up in upside down configuration which is equipped with a cascaded arc plasma source as described in detail in Appendix A. Precursor gases are oxygen, diethyl zinc and additionally for doped films trimethyl aluminum. These liquid precursors are supplied to the reactor chamber utilizing conventional Bronkhorst Hi-Tec mass flow controllers and pressure-controlled bubblers using argon as a carrier gas. For accurate control of precursor feed rate using a bubbler system, a profound knowledge of the precursor vapor pressure, thermal stability, and purity is required.\(^{93-95}\) The vapor pressure curves of both diethyl zinc and trimethyl aluminum are determined as discussed in Appendix B using an experimental set up configured in such a way that any disturbing effects resulting from small leaks, partial decomposition of the reactant, and volatile contaminants in the precursor or the system itself can be corrected for.\(^{96}\)

In order to facilitate the study of plasma processes and film growth, a new laboratory reactor set up with advanced gas handling system, access for various complementary \textit{in-situ} diagnostics and a programmable logical control unit has been designed and constructed as described in detail in Appendix A. Design criteria include a stable and reproducible liquid precursor feed rate and an accurate substrate temperature control, particularly during plasma exposure. Here, the liquid precursors are supplied to the reactor chamber utilizing Bronkhorst Hi-Tec Controlled Evaporation and Mixing systems. The precursor feed rate is controlled in its natural liquid state at ambient conditions using a liquid mass flow meter and subsequently evaporated in a continuous way with the aid of argon as a carrier gas.\(^{97}\)

**C. Material properties, plasma processes and film growth**

Demonstration of low temperature textured ZnO deposition from oxygen, diethyl zinc and additionally for doped films trimethyl aluminum utilizing the expanding thermal plasma technique is discussed.\(^{98}\) Property control is demonstrated, the remote configuration of the expanding thermal plasma technique allows for separate adjustment of plasma production (e.g. arc argon flow), gas phase chemistry (e.g. oxygen flow, trimethyl aluminium flow) and near-substrate conditions (e.g. reactor chamber pressure, temperature), independently affecting intrinsic, i.e. bulk, and application dependent relevant extrinsic transparent conducting oxide quality.\(^{99}\)

Control of film composition is mainly governed by plasma production and gas phase chemistry inherently inducing a significant contribution of film morphology, whereas control of film morphology solely is governed by near-substrate conditions. Especially ratio of zinc to oxygen and reactor chamber pressure appear to be determinative in obtaining ZnO exhibiting the appropriate intrinsic and extrinsic
quality for application in thin film solar cells, i.e. a high electrical conductivity, a high visible transmittance, a textured rough surface morphology and a strong hydrogen plasma resistance.

Film resistivity of undoped ZnO decreases by over two orders of magnitude with an increasing ratio of zinc to oxygen, i.e. decreasing oxygen flow in the reactor chamber. This is mainly attributed to higher charge carrier density; low oxygen flows enhance film substoichiometry, i.e. ratio of zinc to oxygen > 1, due to interstitial zinc atoms and / or oxygen vacancies leading to n-type conductivity.\textsuperscript{100} Also the addition of aluminum drastically reduces film resistivity by over two orders of magnitude to values below 10\textsuperscript{-3} Ωcm; values as low as 6.0 \times 10\textsuperscript{-4} Ωcm have been obtained. Both optical and electrical film properties of aluminum doped zinc oxide (ZnO:Al) films are studied extensively using spectroscopic ellipsometry.\textsuperscript{101}

Film resistivity of undoped ZnO decreases over two orders of magnitude with increasing reactor chamber pressure mainly governed by a pressure dependence of carrier mobility. No large change in carrier density, i.e. film composition, is observed as shown in Fig. 3. Low resistivity values around 10\textsuperscript{-3} Ωcm are obtained. Remarkably, intrinsic quality increases with deposition rate. The increasing carrier mobility
Fig. 4. SEM micrographs of cross section of ETP deposited undoped ZnO films vs. reactor chamber pressure. Substrate temperature 473 K, oxygen flow 50 sccm, arc argon flow 840 sccm.

reflects an improved film structure with less structural defects\(^{102,103}\) and grain boundaries. The carrier mobility obtained is in close vicinity to maximum values reported for intrinsically doped ZnO, taking into account both grain boundary scattering and ionized impurity scattering.\(^{108,104}\)

At a low reactor chamber pressure, pillar-like film morphology is obtained as shown in Fig. 4. Films exhibit the hexagonal wurtzite crystal structure, the grains clearly extend from the substrate to the top of the film which is in accordance with the preferred observation of (002) and (004) diffraction peaks indicating that films are oriented with their c-axis perpendicular to the substrate plane. Single crystallites can be easily distinguished which is more difficult for films deposited at a higher reactor chamber pressure, a transition to pyramid-like film morphology is established.

During the deposition of amorphous silicon pin solar cells from a silane plasma by radio frequency plasma enhanced chemical vapour deposition, the transparent conducting oxide is exposed to atomic and ionic hydrogen. This may reduce the oxide leaving elemental metal particles at the surface significantly lowering the transmittance.\(^{105}\) A mild radio frequency hydrogen plasma treatment is conducted simultaneously on expanding thermal plasma deposited ZnO and the state of the art Asahi U-type fluorine doped tin oxide (SnO\(_2\):F), the total transmittance is measured before and after the treatment as shown in Fig. 5. Whereas the SnO\(_2\):F is reduced noticeably showing a lower transmittance after the treatment, the ZnO stays apparently unaffected.

The suitability of expanding thermal plasma deposited ZnO for application in thin film amorphous silicon pin solar cells is demonstrated\(^{108,109}\) the solar cell performance of appropriate undoped and aluminum
Fig. 5. Total transmittance of ETP deposited undoped ZnO and Asahi U-type SnO$_2$:F before and after hydrogen plasma treatment. Substrate temperature 473 K, oxygen flow 50 sccm, arc argon flow 840 sccm, reactor chamber pressure 250 Pa.

Fig. 6. Spectral response of amorphous silicon pin solar cells grown simultaneously on undoped ETP deposited ZnO and Asahi U-type SnO$_2$:F as a reference.

doped ZnO is comparable with respect to state-of-the-art Asahi U-type SnO$_2$:F. As presented in Fig. 6 a high spectral response has been obtained in the long wavelength regime, indicating an effective light trapping due to optical scattering at the rough ZnO/amorphous silicon interface.

Plasma processes and film growth of expanding thermal plasma deposited textured ZnO is discussed. The expanding thermal plasma is a remote plasma, the downstream properties do not affect the plasma source characteristics due to the large pressure difference of approximately $10^4$ Pa between source and reactor chamber. Consequently, the chemical reactivity is characterized by the argon ion and electron flux emanating from the cascaded arc plasma source. It has been demonstrated that a cascaded arc operated in a low-flow regime behaves similar as one operated in a high-flow regime, typical ion densities in the range $10^{17} - 10^{19}$ m$^{-3}$ and electron temperatures in the range $0.1 - 0.3$ eV are obtained. Figure 7 shows
the result as a function of the arc current and arc argon flow respectively at a distance of 180 mm from the cascaded arc plasma source. The ion flux scales roughly linear with both the arc current and arc argon flow, at 50 A approximately 10% of the arc argon flow is ionised. In all conditions explored an excess of argon ions and low temperature electrons which represent the chemistry taking place is available, i.e. the plasma is underloaded with precursor gases.

The plasma induced decomposition mechanism involves charge exchange with argon ions and consecutive dissociative recombination with electrons emanating from the cascaded arc plasma source. The presence of reactive atomic species, i.e. Zn* (transition 4p^3P_0,1,2 ← 5s^3S_1, 481 nm) and O* (transition 3s^3S_1 ← 3p^3P_{0,1,2}, 777 nm), is confirmed with optical emission spectroscopy measurements shown in Fig. 8. In addition a strong signal representing H* (transition Balmer-α, 656 nm) is present.

Atomic as well as molecular oxygen might directly attribute to the decomposition of diethyl zinc and formation of different bond states i.e. Zn-O, although it is suggested that in the gas phase oxygen will mainly affect the hydrocarbon chemistry. Mass spectrometry measurements reveal CO, H_2O, H_2 and CO_2 as...
main stable reaction products in the plasma induced oxidative decomposition. The formation of the oxidation products H\textsubscript{2}O as well as CO\textsubscript{2} occurs via different reaction pathways compared to CO. The plasma chemistry, i.e. the behavior of atomic oxygen and zinc, is reported to be very similar to combustion chemistry.\textsuperscript{16} The absence of significant amount of residual carbon in the films favours a mechanism involving the dissociation of the Zn-C bonds in the plasma instead of at the surface. Film growth is suggested to proceed by the adsorption of atomic zinc followed by subsequent reaction with oxygen, the deposition rate is directly proportional to the arrival rate of the particular reactive species. It is suggested that the actual oxidation of zinc species and thus the formation of the Zn-O bond occurs at the surface. Film growth starts after a certain critical level of oxygen present as deduced from Fig. 9a, initially a linear relation between film growth and unconsumed oxygen flow is observed atomic zinc becoming the limiting species. Oxygen is consumed in the accompanying hydrocarbon gas phase chemistry before contributing to film growth, which coincides with the trend for oxygen depletion obtained from mass spectrometry measurement as shown in Fig. 9b. With excess of oxygen the depletion becomes constant.

With respect to surface texturing inherently obtained during deposition, it is suggested that film growth might be the interplay of deposition and etching. Considering the preferred [0002] direction of growth, i.e. perpendicular to the substrate plane, etching occurs anisotropically along these basal planes leaving hexagonal shaped pits. Hydrogen species might contribute in the surface texturing\textsuperscript{108,109} fast dry etching of ZnO is recently demonstrated utilizing a remote argon – hydrogen plasma.\textsuperscript{110} (Sub-) surface film modification competitive to etching is observed, predominantly in the early stage of plasma exposure at a low substrate temperature. It is suggested that hydrogen species might contribute in the n-type conductivity considering the low resistivity obtained for undoped ZnO.\textsuperscript{8,9} Besides the ratio and nature of particular reactive species arriving at the substrate surface, an important issue to be considered during surface texture growth is the surface mobility of species arriving at the substrate surface. It is believed that particular zinc species adsorb on the surface in a weakly bounded highly mobile state. A schematic visualisation of surface textured ZnO film growth is represented in Fig. 10.

[Fig. 8. Emission spectrum of oxygen and diethyl zinc containing expanding thermal argon plasma (uncorrected for sensitivity of detector). Substrate temperature 473 K, arc argon flow 840 sccm, arc current 50 A, diethyl zinc flow 5.15 sccm, oxygen flow 50 sccm, reactor chamber pressure 250 Pa.]
III. PROSPECTIVE

The increasing interest in ZnO challenges the development of sophisticated synthesis technologies. Property control of expanding thermal plasma deposited ZnO has been demonstrated opening a wide variety of applications, besides thin film solar cells e.g. architectural glazing, flat panel displays, electro chromic devices, surface acoustic wave devices and gas sensors. In general, present transparent conducting oxide applications are passive, i.e. n-type ZnO is employed as an electrode in different types of devices. The ability of p-type doping of transparent conducting oxides has led this class of materials to the frontier of transparent semiconductors raising the prospect of transparent, high power electronics, e.g. UV light emitters, thin film transistors and light emitting diodes, using an appropriate combination of p- and n-type transparent semiconductors. ZnO is of particular interest offering potential advantages including a
large exciton binding energy. However, despite numerous reports no reproducible high quality p-type ZnO is available yet.

In order to attain the potential offered by ZnO, both high quality n- and p-type material are indispensable, a key requirement for advancing the employment of ZnO is the improved control of doping. The remote configuration of the expanding thermal plasma technique allows separate control of plasma production, gas phase chemistry, and substrate surface treatment facilitating fundamental studies of material properties, plasma processes and film growth. A more profound knowledge of e.g. the plasma processes, plasma composition, surface composition and (sub) surface reactions interacting could benefit a dedicated sophistication of tailoring the material properties. An aid as well an aim in itself is the development and implementation of complementary in-situ diagnostics, e.g. spectroscopic ellipsometry, threshold ionisation mass spectrometry and time resolved cavity ring down spectroscopy. Application of such diagnostics is, obviously, not limited to the expanding thermal plasma technique nor is specific for the study of ZnO film growth.

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CHAPTER 1

EXPANDING THERMAL PLASMA FOR DEPOSITION OF TEXTURED ALUMINUM DOPED ZINC OXIDE WITH FOCUS ON THIN FILM SOLAR CELL APPLICATIONS

ABSTRACT

A new method for low temperature deposition of surface textured aluminum doped zinc oxide is presented utilizing an expanding thermal plasma created by a cascaded arc. Films are deposited at 473 K at a rate of 0.65 – 0.75 nm s⁻¹ exhibiting low resistivity (<10⁻³ Ωcm), high visible transmittance (>80%) and a rough surface texture. First application in amorphous silicon pin solar cells indicates promising light trapping properties.

Doped zinc oxide (ZnO) is a promising transparent conducting oxide (TCO) for silicon based thin film solar cells. It exhibits superior transparency, stronger resistance to hydrogen plasma and requires lower deposition temperatures as compared to the commonly used fluorine-doped tin oxide (SnO$_2$:F) which shows an excellent surface texture enabling effective light trapping properties. Textured ZnO films with different dopants (F, B, Al, Ga, In) have been prepared earlier by several deposition techniques. Here, a new method for low temperature deposition of surface textured aluminum doped zinc oxide (ZnO:Al) is presented utilizing an expanding thermal plasma created by a cascaded arc. It has been shown that this type of remote plasma is capable to produce high growth rates while desired material quality is maintained in hydrogenated amorphous silicon and carbon deposition.

ZnO:Al films are deposited on glass substrates (100x50 mm$^2$) using an Aixtron AIX 2300 MX pre-production reactor set up as shown in Fig. 1. The plasma source is a low flow cascaded arc consisting of three cathodes, a stack of 5 water-cooled circular copper plates insulated from each other by boron nitride rings and an anode plate. A subatmospheric thermal argon plasma is generated in a current controlled dc discharge and subsequently expanded into the low pressure reactor chamber (pressure 250 Pa). Oxygen, diethylzinc (DEZ) and trimethylaluminum (TMA) as a dopant are symmetrically injected at different positions into the reactor chamber. No power is coupled in downstream leading to a low electron temperature (0.2 - 0.3 eV) in the expanding plasma beam. The admixed (co)precursors therefore undergo ionisation via charge exchange and consecutive dissociative recombination downstream of the arc source by respectively argon ions and electrons created in the arc. The mixture of reactive particles flows at subsonic velocities to the substrate where, without any significant ion bombardment, deposition takes place.

ZnO:Al films are deposited at 473 K at a rate of 0.65 – 0.75 nm s$^{-1}$ without almost any optimisation concerning reactor design and deposition conditions. Sheet resistances as low as $7 \Omega \square^{-1}$ have been obtained, corresponding with resistivities below $10^{-3} \Omega \text{cm}$. The total transmittance of films with different thickness is represented in Fig. 2. The optical band gap can be shifted towards higher photon energies due
to higher carrier density with higher doping level. An increased carrier concentration will also be responsible for a shift of the plasma edge in the infrared wavelength region.

As evidenced by XRD the structure of ZnO:Al films deposited at 473 K is hexagonal wurtzite. A preferred observation of (002) and (004) peaks indicates that films are oriented with their c-axes perpendicular to the substrate plane. The typical surface morphology as visualised by the SEM micrograph given in Fig. 3 exhibits a regular rough surface texture. AFM measurements reveal a root mean square roughness of 64 - 84 nm. Feature size as well as root mean square roughness increase with increasing film thickness.

In order to demonstrate the suitability for solar cell applications, an amorphous silicon (a-Si:H) pin solar cell was co-deposited on both ZnO:Al and Asahi U-type SnO$_2$:F in a rf Plasma Enhanced Chemical Vapour Deposition (PECVD) system using standard process recipes. The resulting light I/V data as well as the spectral quantum efficiency of the cells obtained are shown in Fig. 4. The high short circuit current densities up to 16 mA cm$^{-2}$ are obtained mainly due to an effective light trapping in the long wavelength region. The spectral quantum efficiencies of both cells are comparable with a slightly higher value in the range of 400 - 600 nm for the cell on ZnO:Al. Possible differences of p-i(a-Si:H) interface formation on different transparent conducting oxide films have to be taken into account which are reflected in a different
Fig. 4. (a) Light I/V data and (b) the spectral quantum efficiency of a pin a-Si:H solar cell co-deposited on both ZnO:Al and Asahi U-type SnO$_2$:F (i-layer thickness 450 nm).

The lower $V_{oc}$ and $FF$ of the cell on ZnO:Al are probably attributed to the poor electronic quality of the ZnO:Al-p(a-Si:H) contact.  

In summary, surface textured ZnO:Al with low resistivity and high visible transmittance is deposited at 473 K utilizing an expanding thermal plasma. First results on this material in amorphous silicon pin solar cells are promising. More detailed studies of both optical and structural properties in relation to deposition conditions and solar cell applications are in progress.

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ABSTRACT

Aluminum doped zinc oxide films exhibiting a rough surface morphology are deposited on glass substrates utilizing expanding thermal plasma. Spectroscopic ellipsometry is used to evaluate optical and electronic film properties. The presence of aluminum donors in doped films is confirmed by a shift in the zinc oxide band gap energy from 3.32 to 3.65 eV. In combination with transmission reflection measurements in the visible and NIR ranges, charge carrier densities, optical mobilities and film resistivities have been obtained from the free carrier absorption. Film resistivities are consistent with direct measurements, values as low as $6.0 \times 10^{-4} \, \Omega \text{cm}$ have been obtained. The interdependence of electrical conductivity, film composition and film morphology is addressed.

*R. Groenen, E.R. Kieft, J.L. Linden, M.C.M. van de Sanden, J. Electron. Mat., accepted for publication*
I. INTRODUCTION

Zinc oxide (ZnO) is a transparent conducting oxide (TCO) of considerable technological interest for application in amongst others thin film solar cells. It allows for superior transparency, lower deposition temperature, lower cost and less environmental impact compared to the widely used fluorine doped tin oxide (SnO$_2$:F) which shows an excellent surface texture enabling effective light trapping properties. Undoped and doped ZnO films have been deposited by numerous techniques including molecular beam epitaxy, atomic layer deposition, (magnetron) sputtering, chemical vapour deposition, and spray pyrolysis. Low temperature deposition of textured ZnO utilizing expanding thermal argon plasma created by a cascaded arc has been demonstrated. It has been shown that high quality material is obtained, showing excellent performance in thin film amorphous silicon pin solar cells. Here, the effect of aluminum doping on the optical and electronic ZnO film properties is presented using spectroscopic ellipsometry (SE) in combination with transmission reflection measurements in the visible and NIR ranges. Spectroscopic ellipsometry has been demonstrated to be a powerful tool for the analysis of transparent conducting oxide film properties. The interdependence of electrical conductivity, film composition and film morphology is addressed.

II. EXPERIMENTAL DETAILS

Undoped and aluminum doped zinc oxide (ZnO:Al) films are deposited on Corning 1737F glass substrates (100x50 mm$^2$) utilizing an expanding thermal argon plasma created with a cascaded arc as described in detail elsewhere. The plasma source is a wall-stabilised cascaded arc. A subatmospheric thermal argon plasma is generated in a current controlled dc discharge and subsequently expanded into the low pressure reactor chamber. Precursors are oxygen, diethyl zinc (DEZ) and additionally for doped films trimethyl aluminium (TMA) injected downstream by means of punctured rings situated at 65 (i.e. oxygen) and 315 mm (i.e. DEZ / TMA) from the arc outlet, respectively. The liquid precursors are supplied to the reactor chamber utilizing conventional mass flow controllers and pressure-controlled bubblers using argon (purity grade 5.0) as a carrier gas.

Undoped expanding thermal plasma deposited ZnO films exhibit a low resistivity of around $10^{-3}$ Ωcm, a high visible transmittance above 80% and a rough surface morphology similar as obtained using several different deposition techniques or post deposition wet etching of smooth films. To study the effect of aluminum doping, two series of films were deposited, both with a variable trimethyl aluminium flow in the range of 0 to 0.483 sccm. The first series with film thicknesses around 1000 nm served to study the effect of aluminum doping on electrical film properties. Because of the relatively large surface roughness scale, i.e. a root mean square roughness up to 45 nm, it is not straightforward to determine optical constants for these films accurately with spectroscopic ellipsometry. Therefore, a second series with film thicknesses around 100 nm was deposited to determine the optical constants.

All films are deposited at 473 K with a diethyl zinc flow of 5.15 sccm, an oxygen flow of 100 sccm, an argon flow of 840 sccm, an arc power of 3.1 kW and a reactor chamber pressure of 250 Pa. No post-deposition treatment is performed. Note that in contrast to earlier results, for this purpose stoichiometric
ZnO is intended to be deposited as the undoped reference material, i.e. ZnO lacking the presence of intrinsic donors.

Film thickness and sheet resistance are determined with a Tencor P-10 step profiler and a van der Pauw four-point probe, respectively. Surface texture, morphology and crystal structure were studied using atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Spectroscopic ellipsometry measures the change in polarization of light as a function of wavelength when light is reflected from a sample. This polarization change is expressed in terms of the ellipsometric parameters $\Psi$ and $\Delta$.

$$\tan \Psi \cdot e^{i\Delta} = \frac{R_x}{R_y}$$

with $R_x$ and $R_y$ the total Fresnel reflection coefficients respectively parallel and perpendicular to the plane of incidence including interference effects. Data are acquired at an angle of incidence of $75^\circ$ over the spectral range of 245 – 1000 nm with a resolution of 1.6 nm using a Woollam M-2000U rotating compensator ellipsometer. To determine the optical constants in the infrared part of the spectrum, ellipsometric measurements are combined with transmission reflection measurements, using a Perkin Elmer Lambda 900 Ultraviolet/Visible/Near Infrared Spectrometer with a Pela 1020 60 mm integrating sphere. Transmission is measured in a straight-through configuration, whereas reflection is measured under an angle of incidence of $8^\circ$ with respect to the normal. The spectral range of these measurements is 250 – 2500 nm with a resolution of 2.0 nm.

III. RESULTS AND DISCUSSION

SEM micrographs indicate that both undoped and aluminum doped films are strongly textured, see Fig. 1, growing in a columnar structure as described in detail elsewhere. With the addition of trimethyl aluminum a transition from large crystallites to a structure resembling that of sub stoichiometric undoped ZnO films is observed, however the tips of the crystallite columns appear to be more flat then pyramid-like. Root mean square roughness is in agreement with these observations, revealing values decreasing from 45 to 15 nm with the addition of trimethyl aluminum as a dopant. A preferred observation of (002) and (004) peaks indicate films are oriented with their c-axis perpendicular to the substrate plane. From 0.483 sccm trimethyl aluminium supplied to the reactor chamber, additional orientations in the (101) and (100) faces appear. A decreasing normalised intensity of the (002) diffraction peak indicates that the addition of aluminum as a dopant is responsible for a deterioration of film structure, possibly attributed to an interstitial inclusion of the aluminium atoms. ZnO:Al films are generally phase mixtures containing not only the desired phase, i.e. ZnO, but also secondary phases like gahnite, i.e. ZnAl$_2$O$_4$, alumina, i.e. Al$_2$O$_3$, and ZnO$_2$.

No additional phases are detected in the XRD patterns: these phases however might be identified by Transmission Electron Spectroscopy (TEM) and Selected Area electron Diffraction (SAD). To illustrate the effect of film morphology, i.e. average crystallite size, the FWHM (full width at half maximum) corresponding to the predominantly present (002) diffraction peak is plotted. The average crystallite size is inversely proportional to the FWHM, i.e. the narrower the peak, the larger the crystallite size. As it is not straightforward to determine the absolute value of the crystallite size, the FWHM is taken as a measure for the average diameter of the crystallites present in the film.
A simple but appropriate optical model for the visible wavelength range (photon energy < 3 eV) commonly applied for ZnO is the Sellmeier model, consisting of two ideal harmonic oscillators with different resonance frequencies, one in the UV for the above-band edge absorption and one in the IR for the free carrier absorption. In this way only the real part of the complex dielectric function is affected,

\[
\varepsilon_r(E) = 1 + \frac{AE^2}{E^2 - B^2} + \frac{CE^2}{E^2 - D^2} \\
\varepsilon_i(E) = 0
\]

with \( E \) the photon energy in eV, \( A, B, C \) and \( D \) being fit parameters. The optical constants of the surface layer are described as a mixture of 50% ZnO and 50% void (ambient) using the Bruggeman Effective Medium Approximation (BEMA). The optical constants of the bare glass substrate are determined separately. The presence of any voids or additional phases in the bulk layer, formed e.g. by the addition of aluminum dopant to ZnO, is neglected, and the optical properties are considered to be homogeneous in depth. Backside reflections of the glass substrates are generally accounted for. The optical model is used to

Fig. 1. SEM micrographs of cross section of thick ETP deposited undoped and aluminium doped zinc oxide films vs. TMA flow.

Fig. 2. Ellipsometric data and Sellmeier model fit in the range of 1.24 – 3.09 eV (400 – 1000 nm) for thin ETP deposited ZnO:Al film.
determine film thickness, roughness and optical constants for thin ZnO films. An example of a model fit to the experimental ellipsometry data in the range of 1.24 – 3.09 eV (400 – 1000 nm) is shown in Fig. 2. Subsequently, the optical constants are determined ‘point by point’, i.e. in absence of any dispersion relation.

For thin films deposited with trimethyl aluminum flow increasing from 0 up to 0.390 sccm, the photon energy at which absorption starts is increasing as shown in Fig. 3. The plotted energy range is limited to values immediately around the ZnO band gap. For undoped ZnO films the presence of exciton absorption is visible (photon energy ~ 3.4 eV).

Here, the band edge $E_g$ is associated with the energy at which $d\alpha/dE$ reaches a maximum.\textsuperscript{25,26} There appears to be a linear correlation between the shift in band gap energy and trimethyl aluminum flow, $E_g$ increasing from 3.32 to 3.65 eV as shown in Fig. 4. This is in agreement with a quantitative theoretical relation derived,\textsuperscript{27} suggesting that the trimethyl aluminum flow is an appropriate reflection of the aluminum content in the films. The band gap shift can be considered as the net result of a widening due to the blocking

Fig. 3. Energy dependent absorption coefficient for thin ETP deposited ZnO:Al films.

Fig. 4. Optical band gap shift for thin ETP deposited ZnO:Al vs. TMA flow.
of the lowest states in the conduction band (Moss-Burstein shift\textsuperscript{28,29}) and a narrowing due to many-body effects on the conduction and valence bands\textsuperscript{26,30,31}.

At 0.483 sccm trimethyl aluminum flow, a rather dramatic change in the optical film properties occurs. No further increase of the band gap is visible, and an increase of absorption in the film takes place over the entire photon range. The real and imaginary parts of the dielectric function, $\varepsilon_1$ and $\varepsilon_2$ respectively, are shown for the complete measurement range in Fig. 5. Notice that $\varepsilon_1$ shows an increasing negative curvature with increasing doping level at the lower end of the energy range. Through the Kramers-Kronig relationship this trend is consistent with increasing absorption in the infrared part of the spectrum.

The electrical resistivity is directly related to the charge carrier density and mobility. Whereas the mobility mainly depends on the mechanism by which the carriers are scattered by lattice imperfections e.g.
ionised impurity scattering and grain boundary scattering,\textsuperscript{32} the charge carrier density is determined by intrinsic donors (defects) or extrinsic donors (dopants) present.\textsuperscript{33} Absorption by free carriers occurs in the infrared part of the spectrum. To determine the optical constants in the infrared part of the spectrum, ellipsometric measurements are combined with transmission reflection measurements over the spectral range of 250 – 2500 nm. Total transmittance spectra as presented in Fig. 6 confirm an increasing amount of aluminum incorporated in the film as an active dopant with increasing trimethyl aluminum flow. At higher wavelength the transmittance decreases due to free carrier absorption whereas the effective optical band gap becomes wider shifting the lower limit of transmitted light to a lower wavelength.

Ellipsometric and transmission reflection data are fitted together weighting both data types according to their experimental standard deviations. A combination of a Sellmeier term for the above band edge absorption and a Drude oscillator for the free carrier absorption is applied as an optical model, the last one being a single Lorentz oscillator with its center energy fixed at zero.\textsuperscript{34}

![Graph](image)

**Fig. 7.** (a) Electron density \( n_e \) and optical mobility \( m_{opt} \) derived from the Drude oscillator model fit and (b) FWHM of the predominant (002) diffraction peak (b) for thin film ETP deposited ZnO:Al films vs. TMA flow.
\[ \tilde{\varepsilon}(E) = \varepsilon_0(E) + i\varepsilon_r(E) = \frac{A}{E^2 + i\varepsilon_r E} = \frac{\hbar^2}{\varepsilon_0 \rho (E^2 + i\varepsilon_r E)} \]  

(4)

\[ \rho = \frac{m^*}{n_e q^2 \tau} = \frac{1}{q \mu_{opt}} \]  

(5)

with \( \hbar \) Dirac’s constant, \( \varepsilon_0 \) the dielectric constant of free space, \( \rho \) the electrical resistivity in \( \Omega \) cm, \( m^* \) the effective mass of the free electrons, \( n_e \) the charge carrier density, \( q \) the electronic charge, \( \tau \) the relaxation time of the electrons, and \( \mu_{opt} \) the mobility of charge carriers. Regardless of the form the Drude oscillator has two fit parameters, the pair \( A \) and \( B \) is one example and \( \rho \) and \( \tau \) is another. The related parameters of interest are the effective mass of the free electrons, the charge carrier density and mobility of charge carriers. Provided one of these is known, the other two can be determined from the fit parameters, e.g. knowing the effective mass of charge carriers, the carrier concentration and mobility can be determined from \( A \) and \( B \). The effective mass of free electrons used in the calculation of these quantities is taken to be 0.28\( m_e \) of non-degenerate bulk ZnO. A much higher value of 0.50\( m_e \) has been reported by Brehme et al., which is explained by the degeneracy combined with a possible non-parabolic behavior of the conduction band. Note that a higher actual effective mass results in a higher free electron density and lower electron mobility, whereas the resistivities calculated from these values remain unaffected. Charge carrier densities \( n_e \) and optical mobilities \( \mu_{opt} \) derived as parameters in the Drude oscillator model are plotted in Fig. 7 versus trimethyl aluminum flow supplied to the reactor chamber. The observed trends correspond to theoretically expected trends, an increasing dopant concentration leads to an increased free electron density but also to an increase of scattering sites reducing the electron mobility. Addition of trimethyl aluminum to the reactor chamber apparently does not affect average crystallite size significantly as deduced from the FWHM shown in Fig. 3a; the decrease in carrier mobility might mainly result from increased ionised impurity scattering at higher doping levels rather than increased grain boundary scattering. The appearance of orientations in the (101) and (100) faces above 0.483 sccm trimethyl aluminum supplied to the reactor chamber however indicates an additional contribution of increased grain boundary scattering.

Thin film resistivities obtained from charge carrier densities \( n_e \) and optical mobilities \( \mu_{opt} \) derived as parameters in the Drude oscillator model are compared to the measured thin and thick film resistivities as

![Graph](image)

Fig. 8. Drude oscillator model fit derived thin film resistivities and van der Pauw four-point probe measured thin and thick film resistivities corresponding to ETP deposited ZnO:Al films vs. TMA flow.
shown in Fig. 8. The observed correspondence between model fit derived thin film and measured thick film resistivities is explained by the difference between the dc Hall electron mobility and the optical mobility as calculated from the Drude oscillator model. Electrons that are accelerated by a dc voltage may scatter either in the grain bulk (through e.g. phonon, impurity or point defect scattering) or at grain boundaries. Contrary, under the application of a rapidly oscillating electric field (such as at optical frequencies), electrons will not be displaced over a large distance and grain boundary scattering will not be effective. Therefore, for bulk electrons, scattering will only take place by bulk mechanisms and not at grain boundaries. Consequently, as for thick films in contrast to for thin films the grains are relatively large, grain boundary scattering plays only a minor role compared to grain bulk scattering and the optical and dc Hall mobilities will become close. Film resistivities as low as $6.0 \times 10^{-4} \Omega \text{cm}$ have been obtained.

**IV. CONCLUSIONS**

Textured ZnO:Al films are deposited on Corning glass substrates at a temperature of 473 K utilizing expanding thermal plasma. Spectroscopic ellipsometry is used to evaluate optical and electronic film properties. The presence of aluminum donors in doped films is confirmed by a shift in the ZnO band gap energy from 3.32 to 3.65 eV. In combination with transmission reflection measurements in the visible and NIR ranges, charge carrier densities, optical mobilities and film resistivities have been obtained from the free carrier absorption. Film resistivities are consistent with direct measurements, values as low as $6.0 \times 10^{-4} \Omega \text{cm}$ have been obtained. The interdependence of electrical conductivity, film composition and film morphology is addressed.

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CHAPTER 3

PROPERTY CONTROL OF EXPANDING THERMAL PLASMA DEPOSITED TEXTURED ZINC OXIDE WITH FOCUS ON THIN FILM SOLAR CELL APPLICATIONS

ABSTRACT

Property control of expanding thermal plasma deposited textured zinc oxide is demonstrated considering intrinsic, i.e. bulk, and extrinsic transparent conducting oxide quality relevant for application in thin film amorphous silicon pin solar cells. Particularly the interdependence of electrical conductivity, film composition and film morphology, i.e. structure, feature shape and roughness of the surface, is addressed. Control of film composition is mainly governed by plasma production and gas phase chemistry inherently inducing a significant contribution to film morphology, whereas control of film morphology solely is governed by near-substrate conditions. Especially the ratio of zinc to oxygen and the reactor chamber pressure appear to be determinative in obtaining zinc oxide exhibiting the appropriate intrinsic and extrinsic quality, i.e. a high electrical conductivity, a high transmittance, a textured rough surface morphology and a strong hydrogen plasma resistance. The solar cell performance of appropriate undoped and aluminium doped textured zinc oxide inherently obtained during deposition is comparable with respect to Asahi U-type fluorine-doped tin oxide.

* R. Groenen, J. Löffler, J.L. Linden, R.E.I. Schropp, M.C.M. van de Sanden, Thin Solid Films, accepted for publication
CHAPTER 3

I. INTRODUCTION

Owing to unique combined electrical and optical properties, transparent conducting oxides have found a wide variety of applications like thin film solar cells, architectural glazing, display devices, electrochromic devices, and gas sensors. Each application sets different demands on the materials properties. An appropriate measure of the performance of a transparent conducting oxide reflecting its intrinsic bulk quality is the ratio of the electrical conductivity $\sigma$ to the visible absorption coefficient $\alpha$. The quantity $\sigma/\alpha$ is a Figure of Merit for rating transparent conducting oxides, the larger the value of this quantity the better the performance of the transparent conducting oxide. The Figure of Merit generally increases with film thickness, as the intrinsic transparent conducting oxide quality depends on e.g. average crystallite size. Besides intrinsic quality, generally also specific extrinsic quality is required like e.g. mechanical, chemical and thermal durability, surface morphology, and etchability. Extrinsic quality of particular relevance for application as a front contact in thin film amorphous silicon pin solar cells includes an appropriate textured rough surface morphology for effective light trapping and a strong hydrogen plasma resistance. Deposition temperature, cost and environmental impact are other factors that may influence the choice of transparent conducting oxide for any particular application.

Zinc oxide (ZnO) is a transparent conducting oxide of considerable technological interest for application in amongst others silicon based thin film solar cells. It exhibits superior transparency, stronger resistance to hydrogen plasma and allows for lower deposition temperature, lower cost and less environmental impact as compared to the commonly used fluorine-doped tin oxide ($\text{SnO}_2$:F). The latter is preferred in thin film solar cells since it has an excellent pyramid-like surface texture enabling effective light trapping properties. Textured ZnO films have been prepared by several deposition techniques and post deposition wet chemical etching of smooth films. Recently, the utilization of expanding thermal argon plasma created with a cascaded arc is successfully demonstrated for low temperature deposition of textured ZnO.

The electrical conductivity of ZnO is directly related to the charge carrier density and mobility. Whereas the charge carrier density is determined by intrinsic or extrinsic donors present, the mobility mainly depends on the mechanism by which the carriers are scattered by lattice imperfections e.g. ionised impurity scattering and grain boundary scattering. The electrical conductivity thus depends on both composition and morphology of the transparent conducting oxide, which in turn depend on the deposition parameters. Separate control of film composition, i.e. carrier density, and film morphology, i.e. carrier mobility, is highly desirable. Presumably control of film composition will be governed by plasma production and gas phase chemistry, i.e. chemically induced effects, whereas control of film morphology will be particularly determined by near-substrate conditions, i.e. physically induced effects. Both the ratio and nature of particular reactive species arriving at the substrate surface as well as the arrival rate and surface mobility of these species arriving at the substrate surface need to be considered.

Here, the property control of expanding thermal plasma (ETP) deposited textured ZnO is addressed particularly considering the interdependence of electrical conductivity, composition and morphology. As an example, suitability for application as a front contact in thin film amorphous silicon pin solar cells will be demonstrated. This requires a transparent conducting oxide exhibiting the appropriate intrinsic and extrinsic quality.
II. EXPERIMENTAL DETAILS

Undoped and aluminum doped ZnO films are deposited on Corning 1737F glass substrates utilizing an expanding thermal argon plasma created by a cascaded arc as described in detail elsewhere. The plasma source is a wall-stabilised cascaded arc consisting of three cathodes, a stack of circular copper plates insulated from each other by boron nitride rings and a grounded anode plate. The plasma emanates from the cascaded arc through a nozzle, expands supersonically into a low-pressure reactor chamber (20 – 250 Pa), shocks, and flows at subsonic velocity towards a substrate. Precursors are oxygen, diethyl zinc and additionally for doped films trimethyl aluminum (TMA). The liquid precursors are supplied to the reactor chamber utilizing conventional mass flow controllers and pressure-controlled bubblers using argon (purity grade 5.0) as a carrier gas or Bronkhorst Hi-Tec Controlled Evaporation and Mixing systems. With the latter the precursor feed rate is controlled in its natural liquid state at ambient conditions using a liquid mass flow metre and subsequently evaporated in a continuous way with the aid of argon (purity grade 5.0) as a carrier gas. A summary of the deposition conditions explored is shown in Table 1, no post-deposition treatment is performed.

Table 1. ETP deposition conditions explored in relation to ZnO quality.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate temperature</td>
<td>423 – 573 K</td>
</tr>
<tr>
<td>oxygen flow</td>
<td>50 – 120 sccm</td>
</tr>
<tr>
<td>diethyl zinc flow</td>
<td>5.15 sccm</td>
</tr>
<tr>
<td>trimethyl aluminium flow</td>
<td>0 – 0.481 sccm</td>
</tr>
<tr>
<td>arc argon flow</td>
<td>800 – 1400 sccm</td>
</tr>
<tr>
<td>arc power</td>
<td>3.1 kW</td>
</tr>
<tr>
<td>reactor chamber pressure</td>
<td>20 – 250 Pa</td>
</tr>
</tbody>
</table>

The remote configuration of the expanding thermal plasma technique allows for separate adjustment of plasma production (e.g. arc argon flow), gas phase chemistry (e.g. oxygen flow, trimethyl aluminium flow) and near-substrate conditions (e.g. reactor chamber pressure, temperature), independently affecting intrinsic and relevant extrinsic transparent conducting oxide quality. As opposed to direct plasmas, the substrate holder or electrode does not play a role in plasma production implying the absence of any significant ion bombardment and ultraviolet light exposure.

Film thickness and sheet resistance are determined with a Tencor P-10 step profiler and a van der Pauw four-point probe, respectively. All presented films have comparable thickness values around 1200 ± 50 nm to be suitable for application in thin film amorphous silicon pin solar cells.

A Phystech RH 2010 Hall Effect Measurement System is used to determine sheet resistance, carrier density and carrier mobility for a limited number of films. In order to visualise film morphology, a JEOL JSM - 6330 F Field Emission Scanning Electron Microscope (SEM) operated at 5.0 kV is used. X-ray diffractograms (XRD) were recorded with a Philips X-pert SR 5068 powder diffractometer equipped with a Cu Kα source to determine film structure. Root mean square roughness is analysed with a Park Scientific Instruments Autoprobe CP 100µm Atomic Force Microscope operated in contact mode employing...
sharpened nitride, gold coated microlevers. Total and specular transmittance is measured using a Perkin Elmer Lambda Ultraviolet/Visible/Near Infrared double beam spectrophotometer equipped with integrating sphere. Spectrally resolved haze values are determined as the ratio of diffuse to total transmittance, i.e. the ratio of light that is scattered compared to the total intensity of light at the interface. Amorphous silicon pin solar cells were deposited simultaneously on ETP deposited ZnO and Asahi U-type SnO\textsubscript{2}:F as a reference by Radio Frequency (rf) and very high frequency Plasma Enhanced Chemical Vapour Deposition (PECVD) in ultra high vacuum multi chamber systems. Light I/V characteristics of the solar cells were measured at Air Mass 1.5 Global under a solar simulator. Spectral response measurements were performed in order to get more detailed information on the photocurrent generation characteristics of the cells, displayed as external collection efficiency (ECE) spectra.

III. RESULTS AND DISCUSSION

A. Intrinsic zinc oxide quality

Irrespective of the deposition technique, reactor chamber pressure has a remarkable effect on film morphology and thus intrinsic transparent conducting oxide quality. Generally, the resistivity of aluminum doped sputtered ZnO films increases with reactor chamber pressure. A strong decrease in carrier mobility is observed which is mainly attributed to a less compact film structure i.e. increased grain boundary scattering.\textsuperscript{17,18} For ETP deposited ZnO, an opposite trend is observed as shown in Fig. 1. Resistivity decreases over two orders of magnitude with increasing reactor chamber pressure mainly governed by a pressure dependence of carrier mobility. No large change in carrier density, i.e. film stoichiometry, is observed as shown in Fig. 1. Low resistivity values around 10\textsuperscript{-3} \(\Omega\)cm are obtained. Remarkably, intrinsic quality increases with deposition rate. This in contrast to e.g. capacitive coupled plasma deposited ZnO films where the films deposited at a lower rate exhibit a higher carrier density and mobility.\textsuperscript{19}

The increasing carrier mobility reflects an improved film structure with less structural defects\textsuperscript{20,21} and grain boundaries. The carrier mobility obtained is in close vicinity to maximum values reported for intrinsically doped ZnO, taking into account both grain boundary scattering and ionized impurity scattering.\textsuperscript{22,23} At a low reactor chamber pressure, pillar-like film morphology is obtained as shown in Fig. 2. A similar morphology is reported for undoped and aluminum doped sputtered ZnO films.\textsuperscript{10,18,24} XRD diffractograms confirm the hexagonal wurtzite crystal structure; the grains clearly extend from the substrate to the top of the film which is in accordance with the preferred observation of (002) and (004) diffraction peaks indicating that films are oriented with their c-axis perpendicular to the substrate plane. Single crystallites can be easily distinguished which is more difficult for films deposited at a higher reactor chamber pressure, a transition to pyramid-like film morphology is established. Correspondingly, root mean square roughness increases significantly from 20 to 50 nm (not shown) which is characteristic for the different morphologies observed.

Resistivity of ETP deposited ZnO in relation to substrate temperature, oxygen flow, trimethyl aluminium flow, and arc argon flow respectively is shown in Fig. 3. Besides near-substrate conditions, i.e. reactor chamber pressure as shown in Fig. 1, also plasma production and particularly gas phase chemistry affect resistivity within several orders of magnitude. In addition to the resistivity and to illustrate the effect of film morphology, i.e. average crystallite size, the FWHM (full width at half maximum) corresponding to the predominantly present (002) diffraction peak is plotted. The average crystallite size is inversely
Fig. 1. Resistivity $\rho$, charge carrier density $n_e$, and carrier mobility $\mu$ of ETP deposited undoped ZnO films vs. reactor chamber pressure. Substrate temperature 473 K, oxygen flow 50 sccm, arc argon flow 840 sccm.

As shown in Fig. 3a resistivity slightly decreases with increasing substrate temperature. This is mainly attributed to higher carrier mobility; an increasing temperature enhances the average crystallite size of the deposited film as deduced from the FWHM shown in Fig. 3a consequently decreasing grain boundary scattering. However, also a slight widening of the optical band gap shifting the lower limit of transmitted light to a shorter wavelength (Moss-Burstein shift\textsuperscript{25,26}) is obtained with increasing substrate temperature\textsuperscript{28} which indicates a slight increase in charge carrier density affecting the resistivity. As deduced from Fig. 3b, resistivity decreases by over two orders of magnitude with an increasing ratio of zinc to oxygen, i.e. decreasing oxygen flow in the reactor chamber. This is mainly attributed to higher charge carrier density, low oxygen flows enhance film sub stoichiometry, i.e. ratio of zinc to oxygen > 1, due to interstitial zinc atoms and / or oxygen vacancies leading to n-type conductivity.\textsuperscript{23} Also the addition of aluminum drastically
Fig. 2. SEM micrographs of cross section of ETP deposited undoped ZnO films vs. reactor chamber pressure. Substrate temperature 473 K, oxygen flow 50 sccm, arc argon flow 840 sccm.

reduces film resistivity by over two orders of magnitude to values below $10^{-3}$ Ωcm; values as low as 6.0 $10^{-4}$ Ωcm have been obtained as shown in Fig. 3c. In order to study the effect of aluminum as a dopant unambiguously, stoichiometric ZnO is deposited as the undoped reference material. Both optical and electrical film properties of aluminum doped zinc oxide (ZnO:Al) films are studied extensively using spectroscopic ellipsometry as described in detail elsewhere. The enlargement of the average crystallite diameter with increasing oxygen flow as deduced from the FWHM in Fig. 3b indicates also a contribution of the carrier mobility to intrinsic ZnO quality. On the contrary, addition of trimethyl aluminum to the reactor chamber apparently does not affect average crystallite size significantly. Still a decrease in carrier mobility might result from increased ionised impurity scattering at higher doping levels. Despite an increasing average crystallite size as deduced from the FWHM, resistivity increases almost one order of magnitude with increasing arc argon flow as shown in Fig. 3d. This is mainly governed by a lower charge carrier density, i.e. increasing ratio of zinc to oxygen probably attributed to more efficient atomic oxygen generation with an increasing arc argon flow. For ZnO:Al films, a similar trend is observed with arc argon flow. Resistivity increases with increasing arc argon flow without any change in flow of trimethyl aluminum to the reactor chamber, which is attributed to a decreasing amount of aluminum incorporated in the film as an active dopant with increasing arc argon flow. Total transmittance spectra as presented in Fig. 4 are in agreement with these observations. At higher wavelength the transmittance increases due to less free carrier absorption and the effective optical band gap becomes narrower shifting the lower limit of transmitted light to a higher wavelength (Moss-Burstein shift). In aluminium doped sputtered ZnO films the donor efficiency of aluminum was found to be strongly correlated with the oxygen partial pressure.
With increasing deposition temperature, the average grain size increases. This induces a decreasing grain boundary scattering and a change in surface structure as observed in Fig. 5. Films deposited at 473 K show columnar growth and the surface texture originates from the pyramid-like tips of the crystallite columns. At higher substrate temperature a transition from columnar to granular growth is observed, i.e. grains of granular morphology appear on top of the columnar morphology. This suggests an increased nucleation site density i.e. surface mobility of species arriving at the substrate surface. A similar transition in film growth has been reported for films deposited by sputtering in the presence of water vapour. A preferred observation of (002) and (004) diffraction peaks indicates that films are oriented with their c-axis perpendicular to the substrate plane. A shift of the (002) diffraction peak towards lower angle is observed with increasing deposition temperature, attributed to an increased internal compressive stress in the film. In contrast to films deposited at 423 to 523 K which exclusively show the first and second order of the (002) diffraction peak, additional orientations in the (103), (101) and (102) faces are observed for films deposited at 573 K. This is in accordance with the observed transition from columnar to granular growth. Correspondingly, root mean square roughness increases from 30 to 63 nm which is indicative for the different morphologies observed.

With variation of oxygen flow, no change in the preferred columnar growth is present as deduced from XRD diffractograms. All films exclusively show the first and second order of the (002) diffraction peak, no additional orientations are observed. As shown in Fig. 6 an enlargement of the average grain size
together with a change in surface structure is observed with increasing oxygen flow, which might affect grain boundary scattering and consequently carrier mobility. A fairly constant root mean square roughness of 40 to 45 nm is obtained despite a rather significant change in film morphology. Also the presence of aluminum has a peculiar influence on film morphology, despite the fairly constant average crystallite size observed from the FWHM shown in Fig. 3c. A transition from large crystallites to a structure resembling that of sub stoichiometric undoped ZnO films is observed, however the tips of the crystallite columns appear to be more flat than pyramid-like. Root mean square roughness is in agreement with these observations, revealing values decreasing from 45 to 15 nm with the addition of trimethyl aluminum as a dopant. No alumina phase is detected in the XRD diffractograms, which suggests aluminum replaces zinc substitutionally in the hexagonal lattice or aluminum segregates to the non-crystalline region in grain boundaries. A decreasing normalised intensity of the (002) diffraction peak indicates the addition of aluminum as a dopant to be responsible for a deterioration of film structure, possibly attributed to an interstitial inclusion of the aluminum atoms. At 0.481 sccm trimethyl aluminum supplied to the reactor.

Fig. 4. Total transmittance of ETP deposited ZnO:Al films vs. arc argon flow. Substrate temperature 473 K, oxygen flow 100 sccm, TMA flow 0.399 sccm, reactor chamber pressure 250 Pa. Data for undoped ZnO are shown for comparison.
chamber, deterioration of film structure, possibly attributed to an interstitial inclusion of the aluminum atoms. At 0.481 sccm trimethyl aluminum supplied to the reactor chamber, additional orientations in the (101) and (100) faces appear. The transition from columnar to granular growth observed for undoped ZnO films is absent in the case of aluminum doped films in the investigated temperature regime up to 573 K.

For undoped as well as aluminium doped ZnO films, surface structure changes to larger pyramid-like grains with an increasing arc argon flow as shown in Fig. 7. It should be noted that despite an increasing grain size, carrier mobility does not necessarily increase due to structural defects and a less compact and dense film structure.\(^\text{14}\) The transition from columnar to granular growth is achieved now already at a

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Fig. 5. SEM micrographs of cross section of ETP deposited undoped ZnO films vs. substrate temperature. Oxygen flow 50 sccm, arc argon flow 840 sccm, reactor chamber pressure 250 Pa.

Fig. 6. SEM micrographs of surface of ETP deposited undoped and aluminium doped ZnO films vs. oxygen and TMA flow. Substrate temperature 473 K, arc argon flow 840 sccm, reactor chamber pressure 250 Pa.
Fig. 7. SEM micrographs of surface of ETP deposited undoped ZnO films vs. arc argon flow. Substrate temperature 473 K, oxygen flow 50 sccm, reactor chamber pressure 250 Pa.

relatively low deposition temperature of 473 K. In addition to the preferential (002) crystal orientation,

\[
\text{diffraction peaks representing respectively the (103), (101) and (102) faces appear one by one with increasing arc argon flow. A shift of the (002) diffraction peak towards slightly higher angle is observed with increasing arc argon flow, attributed to a decreased internal compressive stress in the film.}^{32}
\]

Root mean square roughness increases from 40 to 75 nm which coincides with the different morphologies observed.

B. Extrinsic zinc oxide quality

Extrinsic transparent conducting oxide quality of particular relevance for application as a front contact in thin film amorphous silicon solar cells includes an appropriate rough surface texture for effective light trapping and a strong hydrogen plasma resistance.\(^3\) As shown in the previous section, control of film morphology and consequently surface texture is established inherently during deposition.

A common way to evaluate surface texture optically is via spectrally resolved haze values representing the ratio of diffuse to total transmittance.\(^31\) The corresponding haze spectra for ETP deposited undoped ZnO in relation to substrate temperature and ZnO:Al in relation to arc argon flow are plotted in Fig. 8 in comparison to Asahi U-type SnO\(_2\):F. The observed trends in film morphology and surface roughness as shown in Fig. 5 and 7 respectively are reflected. The optical haze increases with increasing substrate temperature and arc argon flow exceeding the values corresponding to Asahi U-type SnO\(_2\):F. Scattering is most efficient for short wavelength light. Highest haze values are obtained for films containing both columnar and granular morphology. ZnO:Al films exhibit significantly lower haze than undoped ZnO films obtained at comparable substrate temperature and arc argon flow as deduced from Fig. 8b, which is in accordance with the flat instead of pyramid-like surface texture observed from SEM micrographs. All haze spectra for the ZnO films presented here show approximately a \(\lambda^{-3}\) dependence. Such a behavior can be described by Mie theory, which for Asahi U-type SnO\(_2\):F has been reported to correlate morphological and optical data.\(^34\)

During the deposition of amorphous silicon pin solar cells from a silane plasma by rf PECVD, the transparent conducting oxide is exposed to atomic and ionic hydrogen. This may reduce the oxide leaving elemental metal particles at the surface significantly lowering the transmittance.\(^33\) Recently, etching of ZnO under severe hydrogen plasma treatment is demonstrated.\(^36\) Here, a mild rf hydrogen plasma treatment is
Fig. 8. Haze spectra of ETP deposited (a) undoped ZnO vs. substrate temperature and (b) ZnO:Al vs. arc argon flow in comparison to Asahi U-type SnO$_2$:Fe as a reference. Reactor chamber pressure 250 Pa.

conducted simultaneously on ETP deposited ZnO and the state of the art Asahi U-type SnO$_2$:F (600 s rf power 3 W, hydrogen pressure 2.2 mbar, temperature 503 K), the total transmittance is measured before and after the treatment as shown in Fig. 9. Whereas the Asahi U-type SnO$_2$:F is reduced noticeably showing a lower transmittance after the treatment, the ETP deposited ZnO stays apparently unaffected. It has to be noted that the chemical environment during actual amorphous silicon solar cell deposition is less aggressive, both ETP deposited ZnO and Asahi U-type SnO$_2$:F are hardly affected applying practical deposition conditions. On the contrary, the interaction between transparent conducting oxide and hydrogen containing plasma is of particular relevance with respect to microcrystalline silicon thin film solar cell deposition generally requiring a high hydrogen dilution.$^{17}$

C. Application in thin film amorphous silicon pin solar cells

ZnO films deposited at different substrate temperature, gas phase composition and arc argon flow have been used as a substrate for amorphous silicon pin solar cells. The obtained $I/V$ characteristics are
listed in Tables 2 and 3. All applied ETP deposited ZnO films exhibit comparable resistivity around $10^{-3}$ Ω cm to show the effect of extrinsic quality, i.e. surface texture, unambiguously.

$I/V$ characteristics of cells grown on undoped ZnO deposited at different substrate temperature (columnar to granular growth, pyramid-like surface texture, see Fig. 5) are slightly lower with respect to Asahi U-type SnO$_2$:F. The difference in fill factor can be explained by a contact barrier between the ZnO and p-doped hydrogenated amorphous silicon layer. Because of the chemical stability of ZnO in hydrogen plasma, the introduction of a microcrystalline silicon layer to optimize the fill factor is feasible. As presented in Fig. 10 a high spectral response has been obtained in the long wavelength regime, equivalent to that for cells on Asahi U-type SnO$_2$:F. This indicates an effective light trapping due to optical scattering at TCO substrate.

<table>
<thead>
<tr>
<th>TCO substrate</th>
<th>$j_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>η$_{ini}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO 473 K</td>
<td>18.4</td>
<td>0.79</td>
<td>65</td>
<td>9.5</td>
</tr>
<tr>
<td>ZnO 573 K</td>
<td>17.9</td>
<td>0.79</td>
<td>64</td>
<td>9.1</td>
</tr>
<tr>
<td>Asahi U-type</td>
<td>18.9</td>
<td>0.75</td>
<td>68</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Table 3. $I/V$ characteristics of amorphous silicon pin solar cells grown simultaneously on ZnO:Al deposited at different arc argon flow and Asahi U-type SnO$_2$:F as a reference.

<table>
<thead>
<tr>
<th>TCO substrate</th>
<th>$j_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>η$_{ini}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Al 840 sccm</td>
<td>15.1</td>
<td>0.81</td>
<td>67</td>
<td>8.1</td>
</tr>
<tr>
<td>ZnO:Al 1120 sccm</td>
<td>16.1</td>
<td>0.82</td>
<td>70</td>
<td>9.3</td>
</tr>
<tr>
<td>Asahi U-type</td>
<td>16.8</td>
<td>0.79</td>
<td>73</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Fig. 9. Total transmittance of ETP deposited undoped ZnO and Asahi U-type SnO$_2$:F before and after hydrogen plasma treatment. Substrate temperature 473 K, oxygen flow 50 sccm, arc argon flow 840 sccm, reactor chamber pressure 250 Pa.
Fig. 10. Spectral response of amorphous silicon pin solar cells grown simultaneously on (a) undoped ZnO deposited at different substrate temperature and Asahi U-type SnO₂:F as a reference and (b) ZnO:Al deposited at different arc argon flow and Asahi U-type SnO₂:F as a reference, respectively.

the rough ZnO/amorphous silicon interface which is in agreement with the obtained haze spectra as shown in Fig. 8a. Using ZnO deposited at 323 K and 523 K comparable results have been obtained; no significant difference in solar cell performance is observed despite a change in structure (columnar to granular), feature shape and roughness (30 to 63 nm) of the surface.

ZnO:Al substrates (columnar growth, smooth surface texture) lead to lower solar cell efficiencies compared to undoped ZnO and Asahi U-type SnO₂:F, due to a lower short circuit current as well as fill factor. From spectral response measurements visualised in Fig. 10, two regions of current loss are identified compared to cells deposited on undoped ZnO; a lower response at long wavelengths is attributed to less efficient light trapping which is in agreement with the obtained haze spectra as shown in Fig. 8b, whereas in the short wavelength region current is lost by a higher reflectance from the ZnO/amorphous silicon interface. I/V characteristics of cells grown on ZnO:Al deposited at a higher arc argon flow (granular growth, pyramid-like surface texture) show an increased short circuit current and fill factor. The solar cell
IV. CONCLUSIONS

Property control of ETP deposited textured ZnO is presented, the remote configuration of the ETP technique allows for separate adjustment of plasma production (e.g. arc argon flow), gas phase chemistry (e.g. oxygen flow, trimethyl aluminium flow) and near-substrate conditions (e.g. reactor chamber pressure, temperature), independently affecting intrinsic, i.e. bulk, and application dependent relevant extrinsic transparent conducting oxide quality. Particularly the interdependence of electrical conductivity, film composition and film morphology, i.e. structure, feature shape and roughness of the surface, is addressed. Control of film composition is mainly governed by plasma production and gas phase chemistry inherently inducing a significant contribution of film morphology, whereas control of film morphology solely is governed by near-substrate conditions. Especially the ratio of zinc to oxygen and the reactor chamber pressure appear to be determinative in obtaining ZnO exhibiting the appropriate intrinsic and extrinsic quality, i.e. a high electrical conductivity, a high transmittance, a textured rough surface morphology and a strong hydrogen plasma resistance. The suitability for application in thin film amorphous silicon pin solar cells is demonstrated, the solar cell performance of appropriate undoped and aluminium doped ZnO is comparable with respect to Asahi U-type SnO$_2$:F.

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ABSTRACT

Plasma processes and film growth of textured zinc oxide deposited from oxygen and diethyl zinc utilizing expanding thermal argon plasma created by a cascaded arc is discussed. In all conditions explored an excess of argon ions and low temperature electrons is available which represent the chemistry taking place. The plasma induced decomposition mechanism involves charge exchange with argon ions and consecutive dissociative recombination with electrons emanating from the cascaded arc plasma source. The presence of reactive atomic species, i.e. Zn* and O*, is confirmed with optical emission spectroscopic measurements. The absence of residual carbon in the films favours a mechanism involving the dissociation of the Zn – C bonds in the plasma instead of at the surface. Film growth is suggested to proceed by the adsorption of particular zinc species followed by subsequent reaction with oxygen, the deposition rate is directly proportional to the arrival rate of the particular reactive species. It is suggested that atomic zinc adsorbs on the surface in a weakly bounded highly mobile state. Best intrinsic transparent conducting oxide quality, i.e. film conductivity, is obtained at highest deposition rate.

* R. Groenen, J.L. Linden, M.C.M. van de Sanden, Plasma Processes Polym., accepted for publication
I. INTRODUCTION

Zinc oxide (ZnO) is a transparent conducting oxide of considerable technological interest for application in amongst others surface acoustic wave devices, gas sensors, displays and solar cells. The increasing interest in ZnO challenges the development of sophisticated synthesis technologies allowing for highly tailorable material properties. ZnO films have been deposited by numerous techniques including molecular beam epitaxy, atomic layer deposition, (magnetron) sputtering, chemical vapour deposition, and spray pyrolysis. Plasma-enhanced chemical vapour deposition is utilised only on a limited scale. ZnO can be deposited from zinc acetate, zinc acetylacetonate, dialkyl zinc, or zinc amide by chemical vapour deposition. A commonly used metal organic zinc precursor is diethylzinc. Oxidation can occur by using oxygen, water, alcohol, nitrous oxide, carbon dioxide, or an oxygen containing cyclic compound. ZnO films can also be deposited from alkylzinc alkoxides without any additional oxygen source. The utilization of expanding thermal argon plasma created with a cascaded arc is successfully demonstrated for low temperature deposition of textured ZnO from diethyl zinc and oxygen. Property control of expanding thermal plasma (ETP) deposited textured ZnO is presented, the remote configuration of the ETP technique allows for separate adjustment of plasma production, gas phase chemistry and substrate conditions independently affecting material properties. Here, the relation between plasma processes, film growth and material properties is discussed employing complementary in-situ diagnostics in order to attempt elucidating the deposition mechanism and species dominantly responsible for film growth and surface texturing.

II. EXPERIMENTAL DETAILS

Undoped ZnO films for application as a front contact in thin film amorphous silicon solar cells are deposited on Corning 1737F glass substrates from oxygen and diethyl zinc utilizing an expanding thermal argon plasma. The plasma source is a wall-stabilised cascaded arc consisting of three cathodes, a stack of circular copper plates insulated from each other by boron nitride rings and a grounded anode plate. The plasma emanates from the cascaded arc through a nozzle, expands supersonically into a low-pressure reactor chamber (25 – 250 Pa), shocks, and flows at subsonic velocity towards a substrate. Oxygen and diethyl zinc are injected in the plasma by means of a punctured ring at a distance of 65 and 315 mm from the arc outlet respectively. Diethyl zinc is supplied to the reactor chamber utilizing a pressure-controlled bubbler using argon as a carrier gas or a Bronkhorst Hi-Tec Controlled Evaporation and Mixing system. With the latter the precursor feed rate is controlled in its natural liquid state at ambient conditions using a liquid mass flow metre and subsequently evaporated in a continuous way with the aid of argon (purity grade 5.0) as a carrier gas. Film thickness and sheet resistance are determined with a Tencor P-10 step profiler and a van der Pauw four-point probe, respectively. In order to visualise film morphology, a JEOL JSM - 6330 F Field Emission Scanning Electron Microscope (SEM) is used. Film composition is studied with Energy Dispersive X-ray (EDX) measurements as well as X-ray Photoelectron Spectroscopy (XPS). ETP deposited undoped ZnO films exhibit a low resistivity of around $10^{-3}$ Ωcm, a high visible transmittance above 80% and a rough surface morphology similar as obtained using several different deposition techniques or post deposition wet etching of smooth films.
Langmuir probe measurements are performed in an argon as well as argon – oxygen plasma at a distance of approximately 180 mm from the arc exit to obtain the ion flux which represents the chemistry taking place. These measurements are performed at a constant background pressure in the reactor chamber of 40 Pa. A double cylindrical probe is used, consisting of two tungsten wires with a diameter of 0.25 mm and an exposed length of 5 mm whereas the wires are separated 3 mm. The probe characteristics obtained applying a voltage of -10 to 10 V are analysed by the method proposed by Peterson and Talbot. Reliable application to expanding thermal plasmas is demonstrated, obtained results are in good agreement with Thomson-Rayleigh scattering measurements. Densities are transformed into ion fluxes by integrating over the beam area, the directed velocity at the centre of the plasma beam is assumed from e.g. Doppler-shifted Laser Induced Fluorescence (LIF) measurements to be approximately 1000 m s\(^{-1}\).

In order to gain initial insight into the chemistry, complementary optical emission spectroscopy and mass spectrometry measurements are performed. The total, i.e. non-local, plasma emission at a distance of 30 mm from the substrate surface is collected in the wavelength range 300 – 900 nm with a resolution of 1.5 nm using an Ocean Optics USB2000 Fiber Optic spectrometer. The optical fiber is mounted in front of a quartz window and aligned with the centre of the plasma beam using a focussing lens. A Balzers Prisma QMS 200 F2 mass spectrometer operating at ionization energy of 70 eV is mounted in the reactor pump line sampling gas through a 10 µm pinhole. In this way, only stable reaction products can be detected. All recorded \(m/Z\) signals are normalized to argon to compensate for fluctuations of pressure and temperature, and corrected for the background contribution of this specific \(m/Z\) value. Different gaseous species are calibrated for, providing the correlation between the partial gas pressure in the reactor chamber and the resulting ion current as measured using mass spectrometry.

III. RESULTS AND DISCUSSION

A. Plasma chemistry aspects

The ETP is a remote plasma, the downstream properties do not affect the plasma source characteristics due to the large pressure difference of approximately 10\(^4\) Pa between source and reactor chamber. Consequently, the chemical reactivity is characterized by the argon ion and electron flux emanating from the cascaded arc plasma source. It has been demonstrated that a cascaded arc operated in a low-flow regime behaves similar as one operated in a high-flow regime, typical ion densities in the range \(\sim 10^{17} – 10^{19} \text{ m}^{-3}\) and electron temperatures in the range \(\sim 0.1 – 0.3 \text{ eV}\) are obtained. Figure 1 shows the result as a function of the arc current and arc argon flow respectively at a distance of 180 mm from the cascaded arc plasma source. The ion flux scales roughly linear with both the arc current and arc argon flow, at 50 A approximately 10% of the arc argon flow is ionised. Note that the ion flux is independent of the distance to the arc exit, which indicates the absence of significant recombination between argon ions and electrons.

Decomposition of diethyl zinc can occur either thermally, directly stimulated by the plasma, or through reaction with oxygen due to its pyrophoric nature. Thermal decomposition starts at temperatures of approximately 573 K, involving a homolytic dissociation of the Zn – C bond leading to the production of ethane, ethene and n-butane. The gaseous oxidation of diethyl zinc is a fast autocatalytic chain reaction with a slow initiation reaction producing stable peroxide. Spontaneous decomposition of diethyl zinc, \(\text{Zn(C}_2\text{H}_5)_2\), in absence of either oxygen or plasma exposure is negligible.
The low values of the electron temperature (< 0.3 eV) indicate a limited dissociative power, electron-induced dissociation of any molecular gas added to the argon plasma is considered to account for a minor contribution. Bond dissociation energies for the first and second diethyl zinc Zn – C bond amount 2.2 and 0.95 eV respectively. The proposed plasma induced diethyl zinc decomposition mechanism involves a charge exchange reaction of an argon ion with a diethyl zinc molecule directly followed by the dissociative recombination of $\text{Zn(C}_2\text{H}_5)^+$ or $\text{C}_2\text{H}_5^+$ with an electron, i.e.,

\begin{align*}
\text{charge exchange} \\
\text{Ar}^+ + \text{Zn(C}_2\text{H}_5) \rightarrow \text{Zn(C}_2\text{H}_3)^+ + \text{C}_2\text{H}_5 + \text{Ar} \\
\text{Ar}^+ + \text{Zn(C}_2\text{H}_5) \rightarrow \text{Zn(C}_2\text{H}_3) + \text{C}_2\text{H}_5^+ + \text{Ar} \\
\text{dissociative recombination} \\
\text{Zn(C}_2\text{H}_3)^+ + e^- \rightarrow \text{Zn} + \text{C}_2\text{H}_5
\end{align*}
\[ \text{C}_2\text{H}_4^+ + \text{e}^- \rightarrow \text{C}_2\text{H}_2 + \text{H} \] \quad (4)
\[ \text{C}_2\text{H}_3^+ + \text{e}^- \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{H} \] \quad (5)
\[ \text{C}_2\text{H}_7^+ + \text{e}^- \rightarrow \text{CH}_3 + \text{CH}_2 \] \quad (6)

The charge exchange reaction is dissociative as the parent ion Zn(C\text{2H}_3)_2^+ is unstable,\(^{42}\) favourably breaking the Zn – C bond. Reactive species formed in the dissociative recombination via (3-6) have a lifetime much shorter than the residence time of the gases in the reactor chamber (typically 1200 ms); they either deposit on the walls (typical loss time 0.5 – 50 ms, depending on the sticking probability) or react in the gas phase. With an excess of (Ar\(^+\), e\(^-\)) consecutive charge exchange occurs via (7-8) directly followed by dissociative recombination via (3-6),

\[ \text{Ar}^+ + \text{Zn(C}_2\text{H}_3) \rightarrow \text{Zn}(\text{C}_2\text{H}_3)_2^+ + \text{Ar} \] \quad (7)
\[ \text{Ar}^+ + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4^+ + \text{Ar} \] \quad (8)

The homolytic dissociation of the Zn – C bond leaves, besides atomic zinc, alkyl radicals which contribute to the production of e.g. ethane, ethene, ethyne and n-butane, initiating hydrocarbon gas phase chemistry,

\[ \text{C}_2\text{H}_1 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 \] \quad (9)
\[ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_{10} \] \quad (10)
\[ \text{C}_2\text{H}_1 \rightarrow \text{C}_2\text{H}_4 + \text{H} \] \quad (11)
\[ \text{C}_2\text{H}_3 + \text{H} \rightarrow \text{C}_2\text{H}_6 \] \quad (12)
\[ \text{CH}_4 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \] \quad (13)
\[ \text{CH}_3 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H} \] \quad (14)
\[ \text{CH}_2 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{H} \] \quad (15)

Optical emission spectroscopic as well as mass spectrometric measurements support the postulated mechanism. The presence of reactive atomic species, i.e. Zn\(^+\) (transition 4p\(^3\)P\(_2\) \leftrightarrow 5s\(^5\)S\(_0\), 481 nm), is confirmed with optical emission spectroscopic measurements. It is expected that the observed emission is an appropriate indication of the dissociative recombination of ethyl zinc (3) ions leading to these species whereas electron induced excitation, i.e. dissociation, is absent. Mass spectrometric measurements in this configuration do not show any zinc related fragments, indicating the absence of Zn(C\text{2H}_3)_2, Zn(CH\text{2}_3)_2 and Zn\text{2H}_2 in the gas phase. Under plasma exposure, diethyl zinc is completely decomposed. Main species detected are C\text{2H}_6, C\text{2H}_4, C\text{2H}_2, and H\(_2\) as represented in Fig. 2. Note that the fragment C\text{2H}_7\(^+\) can be attributed to both C\text{2H}_4 and C\text{2H}_6 to distinguish its contribution to these species, the ratio C\text{2H}_7\(^+\)/C\text{2H}_4\(^+\) has been plotted as C\text{2H}_4\(^+\) is solely attributed to C\text{2H}_4. The formation of lower hydrocarbons is stimulated with increasing arc current or arc argon flow i.e. increasing amount of (Ar\(^+\), e\(^-\)) emanating from the arc. Under specific conditions, i.e. at a low arc current, small amounts of CH\text{3H}_6, C\text{2H}_4, C\text{2H}_2 are present.

In the presence of oxygen, i.e. during zinc oxide deposition, (Ar\(^+\), e\(^-\)) emanating from the cascaded arc will be partly consumed to produce atomic oxygen involving a charge exchange reaction of an argon ion with an oxygen molecule directly followed by the dissociative recombination of O\text{2}\(^+\) with an electron\(^{41}\) i.e.,

\[ \text{Ar}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{Ar} \quad k \approx 4.6 \times 10^{-17} \text{ m}^3 \text{s}^{-1} \] \quad (16)
\[ \text{O}_2^+ + \text{e}^- \rightarrow \text{O} + \text{O} \quad k \approx 1.95 \times 10^{-13} \text{ m}^3 \text{s}^{-1} \] \quad (17)
Fig. 2. Different reaction product related fragments detected with mass spectrometry in the plasma induced decomposition of diethyl zinc versus arc current. Substrate temperature 473 K, arc argon flow 840 sccm, diethyl zinc flow 5.15 sccm, reactor chamber pressure 250 Pa.

The addition of oxygen does not affect the argon ion flux emanating from the cascaded arc plasma source, it does affect the argon ion flux downstream since oxygen consumes (Ar⁺, e⁻). Note that the effective ion mass is equal to the argon ion mass and the obtained ion flux equals the argon ion flux. The rate coefficient for the dissociative recombination of the molecular oxygen ion via (17) is several orders of magnitude higher than that of the charge exchange with an argon ion via (16), resulting in a rather low molecular oxygen ion density. Since the charge exchange of an argon ion with atomic oxygen is slow, the atomic oxygen ion density is low also. In Fig. 3 the argon ion flux versus oxygen flow at a distance of 180 mm from the cascaded arc plasma source in absence of diethyl zinc is shown. It is observed that overloading does not result in a complete depletion of argon ions. The plasma beam width does decrease with increasing oxygen flow as deduced from Fig. 3, suggesting that the oxygen mainly reacts with ions.

Fig. 3. Argon ion flux versus oxygen flow as obtained from Langmuir probe measurements. Reactor chamber pressure 40 Pa.
situated at the edge of the plasma and at the centre of the beam mainly argon is present. Similar observations have been reported in the past for oxygen as well as hydrogen. 34,44,45

Atomic as well as molecular oxygen might directly attribute to the decomposition of diethyl zinc and formation of different bond states i.e. Zn-O, although it is suggested that in the gas phase oxygen will mainly affect the hydrocarbon chemistry, e.g.,

\[
\begin{align*}
\text{C}_2\text{H}_5 + \text{O} & \rightarrow \text{CH}_2\text{O} + \text{CH}_3 \\
\text{C}_2\text{H}_4 + \text{O} & \rightarrow \text{CH}_2\text{CHO} + \text{H} \\
\text{C}_2\text{H}_5 + \text{O} & \rightarrow \text{C}_2\text{H}_6 + \text{OH} \\
\text{CH}_3 + \text{O} & \rightarrow \text{CH}_2\text{O} + \text{H} \\
\text{CH}_2\text{O} + \text{O} & \rightarrow \text{CO} + \text{OH} + \text{H} \\
\text{CH}_3\text{O} + \text{O} & \rightarrow \text{HCO} + \text{OH} \\
\text{CH}_3\text{CHO} + \text{O} & \rightarrow \text{CH}_3\text{CO} + \text{OH} \\
\text{CH}_3\text{CO} + \text{O} & \rightarrow \text{CO}_2 + \text{CH}_3 \\
\text{CH}_2 + \text{O} & \rightarrow \text{CO} + \text{H} + \text{H} \\
\text{CH} + \text{O} & \rightarrow \text{CO} + \text{H}
\end{align*}
\]

The presence of reactive atomic species, i.e. Zn* (transition \(4p^3P \rightarrow 5s^3S_1, 481 \text{ nm}\)) and O* (transition \(3s^3S_2 \rightarrow 3p^3P_{0,1,2}, 777 \text{ nm}\)), is confirmed with optical emission spectroscopic measurements shown in Fig. 4. Note that a strong signal representing H* (transition Balmer-\(\alpha\), 656 nm) is present. No emission related to carbon containing atomic species, e.g. CH, CH\(_2\), as well as any molecular species, e.g. CO, CO\(_2\) is collected.

Mass spectrometric measurements do not show any zinc related fragments, indicating the absence of Zn(C\(_2\)H\(_5\))\(_2\), Zn(CH\(_3\))\(_2\), ZnH\(_2\), Zn(O\(_2\)C\(_2\)H\(_5\))\(_2\), Zn(OCH\(_3\))\(_2\), Zn(OH)\(_2\) and ZnO as abundant gaseous products.
Main products detected in the plasma induced oxidative decomposition are CO, H$_2$O, H$_2$ and CO$_2$, see Fig. 5. The formation of the oxidation products H$_2$O as well as CO$_2$ occurs via different reaction pathways compared to CO, which is confirmed by the trends observed in Fig. 5b. Under specific conditions, i.e. at very low arc current, small amounts of C$_2$H$_5$OH and possibly CH$_2$O are present. The latter is considered to be an intermediate oxidation product which is immediately converted to CO via (22,23). Not detected are CH$_2$O, CH$_3$OH, CH$_3$OCH$_3$, C$_2$H$_5$OC$_2$H$_5$ and C$_2$H$_5$O, although these species can still be present in a very low amount or as a consumed intermediate. Note that the detected stable reaction products do not necessarily originate from the primary chemistry; they can also be formed in secondary chemistry, i.e. after recirculation in the background. The plasma chemistry, i.e. the behavior of atomic oxygen and zinc, is reported to be very similar to combustion chemistry. 

Fig. 5. Different reaction product related fragments detected with mass spectrometry in the plasma induced oxidative decomposition of diethyl zinc versus (a) arc current and (b) oxygen flow, respectively. Substrate temperature 473 K, arc argon flow 840 sccm, diethyl zinc flow 5.15 sccm, reactor chamber pressure 250 Pa.
B. Surface chemistry aspects

The absence of significant amount of residual carbon in the films as proved with XPS favours a mechanism involving the dissociation of the Zn – C bonds in the plasma instead of at the surface. A similar observation is reported in the inductively coupled plasma deposition of carbon-free zinc films from diethyl zinc at low power density. Under particular deposition conditions, i.e. the configuration of precursor injection in the plasma, agglomerates are observed on top of the film surface as shown in Figure 6. From EDX measurements exhibiting a penetration depth of approximately 1 µm, a relatively high carbon content compared to the film is observed in these agglomerates finding their origin in the gas instead of plasma phase, i.e. involving incomplete precursor decomposition. Note that the displayed film carbon content mainly originates from the surface after exposure to ambient atmosphere.

![Image of agglomerates on top of ETP deposited aluminum doped ZnO film surface and carbon content of film and surface respectively as determined by EDX. Substrate temperature 473 K, arc argon flow 840 sccm, arc current 50 A, diethyl zinc flow 5.15 sccm, oxygen flow 100 sccm, reactor chamber pressure 250 Pa.](image-url)

Fig. 6. Agglomerates on top of ETP deposited aluminum doped ZnO film surface and carbon content of film and surface respectively as determined by EDX. Substrate temperature 473 K, arc argon flow 840 sccm, arc current 50 A, diethyl zinc flow 5.15 sccm, oxygen flow 100 sccm, reactor chamber pressure 250 Pa.
The role of oxygen is not completely understood yet, changing the ratio zinc to oxygen in the gas phase however significantly affects deposition rate, film growth and material quality as recently demonstrated. It is suggested that the actual oxidation of zinc species and thus the formation of the Zn – O bond occurs at the surface. A similar mechanism is postulated in the capacitively coupled plasma deposition of ZnO films from diethyl zinc and oxygen. The question arises, whether molecular or atomic oxygen determines film growth. Film growth starts after a certain critical level of oxygen present as deduced from Fig. 7a, initially a linear relation between film growth and unconsumed oxygen flow is observed atomic zinc becoming the limiting species. Oxygen is consumed in the accompanying hydrocarbon gas phase chemistry before contributing to film growth, which coincides with the trend for oxygen depletion obtained from mass spectroscopy measurement as shown in Fig. 7b.

With excess of oxygen the depletion becomes constant. The reaction product related fragments (Fig. 5) as well as the depletion (Figure 7) derived from mass spectrometric measurements support the simplified global reaction for ZnO deposition,

Fig. 7. (a) Deposition rate and resistivity $\rho$ of ETP deposited undoped zinc oxide films versus oxygen flow together with (b) oxygen depletion as obtained from mass spectrometry measurements. Substrate temperature 473 K, arc argon flow 840 sccm, arc current 50 A, diethyl zinc flow 5.15 sccm, reactor chamber pressure 250 Pa.
\[ \text{Zn(C}_2\text{H}_5\text{)}_2 + 5\text{O}_2 \rightarrow 4\text{CO} + 5\text{H}_2\text{O} + \text{ZnO} \]  
\tag{28}

in which the consumed diethyl zinc to oxygen ratio amounts one-to-five. No evidence is present for complete stoichiometric combustion opposed to electron-induced dissociating plasmas,\(^\text{[16]}\) i.e.,

\[ \text{Zn(C}_2\text{H}_5\text{)}_2 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 5\text{H}_2\text{O} + \text{ZnO} \]  
\tag{29}

Note that still an excess of oxygen in the reactor chamber is required, i.e. a ratio diethyl zinc to oxygen higher than one-to-five, in order to obtain high quality ZnO films.

With respect to surface texturing inherently obtained during deposition\(^\text{[27,28]}\) it is suggested that film growth might be the interplay of deposition and etching. Considering the preferred [0002] direction of growth, i.e. perpendicular to the substrate plane, etching occurs anisotropically along these basal planes leaving hexagonal shaped pits. It is postulated that hydroxyl species may be responsible for surface texturing.
growth.\textsuperscript{54,58} Detection of these species is demonstrated using cavity ring down spectroscopy.\textsuperscript{49,50} The presence of hydroxyl species originating from the oxygen induced hydrocarbon gas phase chemistry is proved during the deposition of silicon oxide from oxygen and hexamethyldisiloxane utilising an expanding thermal argon plasma.\textsuperscript{51} Also hydrogen species might contribute in the surface texturing,\textsuperscript{51,52} fast dry etching of ZnO is recently demonstrated utilizing a remote argon – hydrogen plasma as described in detail elsewhere.\textsuperscript{53}

Besides the ratio and nature of particular reactive species arriving at the substrate surface, an issue to be considered during surface texture growth is the surface mobility of species arriving at the substrate surface. It is believed that particular zinc species adsorb on the surface in a weakly bounded highly mobile state; lowering the substrate temperature results in a lower surface mobility and consequently smaller grains, increased grain boundary scattering and reduced intrinsic transparent conducting oxide quality, i.e. film conductivity, as show in Fig. 8a and described in more detail elsewhere.\textsuperscript{28} Considering the low resistivity of around $10^{-3}$ Ω cm, hydrogen species might contribute in the n-type conductivity.\textsuperscript{54,55} Generally no effect of temperature on deposition rate is observed indicating a limitation of the reactive species arriving at the substrate, i.e. film growth is gas phase diffusion limited, as shown in Fig. 8a. The deposition rate is directly proportional to the arrival rate of the particular reactive species. At a high reactor chamber pressure the partial pressure of reactive species near the substrate surface is high due to the decreased width of the plasma beam. With the absence of any kinetic limitation, the development of existing grains is preferred over the nucleation of new grains, i.e. the particular reactive species stick in the place where they intercept the substrate surface, the arrival rate of species dominates its surface mobility.

This is in agreement with the observed trend shown in Fig. 8b, best intrinsic transparent conducting oxide quality, i.e. film conductivity, is obtained at highest deposition rate. A schematic visualisation of surface textured ZnO film growth is represented in Fig. 9.

\begin{center}
\includegraphics[width=\textwidth]{fig9.png}
\end{center}

\textit{Fig. 9. ETP surface textured ZnO film growth.}

\textbf{IV. CONCLUSIONS}

Plasma processes and film growth of textured ZnO deposited from oxygen and diethyl zinc utilizing expanding thermal argon plasma created by a cascaded arc is discussed. In all conditions explored an excess of argon ions and low temperature electrons which represent the chemistry taking place is available as deduced from Langmuir probe measurements performed in an argon as well as argon – oxygen plasma, i.e.
the plasma is underloaded with precursor gases. The plasma induced decomposition mechanism involves charge exchange with argon ions and consecutive dissociative recombination with electrons emanating from the cascaded arc plasma source. The presence of reactive atomic species, i.e. Zn* and O*, is confirmed with optical emission spectroscopic measurements. Mass spectrometric measurements reveal CO, H₂O, H₂ and CO₂ as main stable reaction products in the plasma induced oxidative decomposition. The formation of the oxidation products H₂O as well as CO₂ occurs via different reaction pathways compared to CO. The absence of residual carbon in the films favours a mechanism involving the dissociation of the Zn – C bonds in the plasma instead of at the surface. Film growth is suggested to proceed by the adsorption of particular zinc species followed by subsequent reaction with oxygen, the deposition rate is directly proportional to the arrival rate of the particular reactive species. Best intrinsic transparent conducting oxide quality, i.e. film conductivity, is obtained at highest deposition rate. Besides the ratio and nature of particular reactive species arriving at the substrate surface, an important issue to be considered during surface texture growth is the surface mobility of species arriving at the substrate surface. It is suggested that atomic zinc adsorbs on the surface in a weakly bounded highly mobile state.

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CHAPTER 5

DRY ETCHING OF SURFACE TEXTURED ZINC OXIDE USING A REMOTE ARGON – HYDROGEN PLASMA

ABSTRACT

A new method for fast dry etching of inherently textured zinc oxide using a remote argon-hydrogen plasma created by a cascaded arc is presented, obtaining etch rates over 10 nm s⁻¹. Atomic hydrogen is considered to be the reactive species responsible for the etching process, the excess of molecular hydrogen in the gas phase does not contribute to the etching. Furthermore, using in-situ spectroscopic ellipsometry (sub-) surface film modification competitive to etching is observed.

I. INTRODUCTION

Zinc oxide (ZnO) is a transparent conducting oxide (TCO) of considerable technological interest for application in amongst others surface acoustic wave devices, gas sensors, displays, solid state lightning and solar cells. Besides the need for improved film growth techniques, a proper etching technique is imperative, in order to fabricate optoelectronic devices. Opposite to numerous wet-etching chemistries for ZnO, just a few attempts on dry ZnO etching have been reported involving ion-assisted halogen- or carbon-based chemistries. The observed etch rates are generally consistent with the vapour pressures of the expected etch products, e.g., a volatile metal (Zn) organic compound in case of a carbon-based chemistry.

Considering the recently recognized role of hydrogen in ZnO film modification with respect to n-type conductivity and surface texture, here a new method for fast dry etching is shown using a remote argon-hydrogen plasma in the absence of significant ion bombardment. Moreover, the investigation on the interaction between ZnO films and hydrogen-containing plasmas becomes particularly relevant with respect to the deposition of microcrystalline silicon for thin film-solar cell applications, which commonly requires a high dilution of silane in hydrogen. Two-photons Absorption Laser Induced Fluorescence (TALIF) experiments run in similar plasma conditions as those described in this contribution have allowed measuring an atomic hydrogen density in the order of $10^{18}$ m$^{-3}$. Here, the role of a remote hydrogen-containing plasma in the etching and/or surface modification of ZnO films as a function of the substrate temperature is investigated. Experimental evidence for etching and material properties modification of ZnO is provided by in-situ spectroscopic ellipsometric studies.

II. EXPERIMENTAL DETAILS

Undoped surface textured ZnO films, are deposited from oxygen and diethylzinc utilizing an argon-fed expanding thermal plasma generated in a cascaded arc as described in more detail elsewhere. The films, deposited on polished crystalline silicon (111) substrates at a temperature of 473 K, are characterized by a low resistivity of about 10$^{-3}$ Ωcm, a high visible transmittance above 80% and a rough surface morphology similar to the one obtained using other deposition techniques or post deposition wet etching of originally flat films. No residual carbon in the films is detected by means of X-ray photoelectron spectroscopy. Therefore we can exclude a priori the etching of zinc via the formation of metal-organic compounds in the upcoming discussion of the etching experiments.

The ZnO film etching experiments are performed in a similar expanding thermal plasma set up. The remote configuration of this technique allows separate control of plasma production, gas phase chemistry, and substrate surface treatment. A sub-atmospheric thermal argon plasma is generated in a cascaded arc ($p = 0.3 - 0.4 \times 10^5$ Pa, $I_{arc} = 30-90$ A) and expands supersonically into the low pressure (100 Pa) reactor chamber. At 50 mm from the arc outlet, the hydrogen is injected in the plasma by means of an injection ring. No power is coupled in downstream leading to a low electron temperature (0.2 - 0.3 eV) in the expanding beam. Electron-induced molecular dissociation is unlikely to occur and the plasma chemistry is dominantly controlled by the ($\text{Ar}^+$, e$^-$) fluence emanating from the arc. The dissociation of hydrogen
under these conditions occurs according to the following reactions of charge exchange (1) and dissociative recombination (2),

$$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} \quad 1.2 \times 10^{14} \text{ m}^3 \text{s}^{-1} \quad (1)$$

$$\text{ArH}^+ + \text{e}^- \rightarrow \text{Ar} + \text{H}^* \quad 10^{13} \text{ m}^3 \text{s}^{-1} \quad (2)$$

The mixture of reactive particles flows at subsonic velocities towards the substrate placed at 600 mm from the nozzle where, without any significant ion bombardment, \(^{20,24}\) ZnO etching takes place.

*In-situ* real-time Spectroscopic Ellipsometry (SE) is applied to evaluate the etching process in terms of etch rate and (sub-)surface modification of the material properties. The ellipsometric angles \(\Psi\) and \(\Delta\) were acquired at an angle of incidence of 68° over the spectral range of 245 – 1000 nm with a resolution of 1.6 nm using a Woollam M-2000F rotating compensator ellipsometer; spectra were recorded with an acquisition time of 0.20 – 4.1 s and a repetition time of 0.36 – 6.5 s corresponding to a variation of 1.8 – 3.8 nm in ZnO film thickness.

III. RESULTS AND DISCUSSION

In the absence of plasma exposure, i.e., in an argon-hydrogen gas mixture, as well as under plasma exposure without any hydrogen addition, no etching is observed in the temperature range 323 – 573K. In the presence of argon-hydrogen plasma, the etch rate saturates at 4 sccs of hydrogen (see Fig.1), due to a limitation in the concentration of the reactive etching species. This is supported by the decrease of the etch rate occurring at lower arc current or argon flow rate, as reported also in Fig. 1: a lower \((\text{Ar}^+, \text{e}^-)\) fluence emanating from the arc limits the production of atomic hydrogen, according to (1,2). Atomic hydrogen, therefore, is the reactive species, whereas the excess of molecular hydrogen in the gas phase does not contribute to the etching. A maximum effective etch rate of about 5 nm s\(^{-1}\) occurs around 2 sccs of hydrogen, coinciding with a maximised amount of atomic hydrogen arriving at the substrate surface. A

![Fig. 1](image-url) ZnO etch rate versus hydrogen flow rate for different \((\text{Ar}^+, \text{e}^-)\) fluences emanating from the cascaded arc plasma source.
postulated etching mechanism may involve the removal of O by means of H and subsequent elimination of Zn in its metallic state, although the elimination of Zn via the formation of ZnH₂ can not be excluded.

We can estimate the hydrogen atom reaction probability \( \beta \) at the ZnO surface from the mass removal rate \( \Gamma_{\text{etch}} \), as obtained from the etching rate \( R_{\text{etch}} \) and the density of the ZnO film \( (\rho = 5.6 \text{ g cm}^{-3}) \), and the atomic hydrogen density \( (n) \), according to (3), under the hypothesis that the hydrogen fully contributes to the etching process,

\[
\Gamma_{\text{etch}} = \rho R_{\text{etch}} = \frac{1}{4} n v \beta \left(\frac{1}{2} - \beta\right)
\]  

(3)

where \( v \) is the thermal velocity of the hydrogen atom, estimated to be around 1000 m s\(^{-1}\). We obtain a surface reaction probability of 0.9, suggesting a very high efficiency of H in etching ZnO films.

The optical model applied to the SE data is shown as inset in Fig. 2a and consists of a semi-infinite crystalline silicon substrate, a native oxide layer (2-3 nm thick), ZnO bulk film and surface layer roughness. The optical constants of the silicon substrate with native oxide are determined separately for each

\[\text{Fig. 2. Evolution of ZnO (a) film thickness and (b) surface roughness during plasma exposure at different substrate temperature.}\]
DRY ETCHING OF SURFACE TEXTURED ZINC OXIDE...

Fig. 3. Refractive index (n) and absorption coefficient (k) of ZnO films during plasma exposure at different substrate temperatures.

Fig. 2 shows that the ZnO film thickness decrease as a function of the plasma exposure time as well as the surface roughness evolution at different stages of the plasma process, for the substrate temperatures of 323 and 573K. Whereas at high temperature the film thickness decreases linearly in time and a moderate surface roughness develops, i.e. an increasing top layer thickness and void fraction are observed, a low substrate temperature witnesses a non-linear thickness decrease and a considerable surface roughening at the early stage of plasma exposure (~ 300 s). Moreover, a change in the optical constants $n$ and $k$ of the films compared to the untreated material is observed mainly at 323K, see Fig. 3a. These results clearly point out to a competition between etching and (sub-)surface modification at low substrate temperature.
With variation of substrate temperature in the range 323 – 573K, shown in Fig. 4, an overall activation energy of $0.23 \pm 0.01$ eV ($22.3 \pm 1.0$ kJ mol$^{-1}$) is determined, as calculated by averaging over the total exposure to the plasma of ZnO films at different substrate temperatures. This value is indicative for surface kinetics control, i.e. a limitation of formation and removal of reaction products from the substrate surface. Furthermore, the initial non-linear decrease of film thickness in time at low substrate temperature results in a higher initial activation energy of $0.31 \pm 0.01$ eV ($29.8 \pm 1.1$ kJ mol$^{-1}$) confirming a less pronounced etching at the early stage of plasma exposure, i.e. (sub-) surface modification competitive to etching. The initial-to-overall ratio of activation energy approaches unity as the substrate temperature increases. Once a modified and presumably hydrogen-rich (sub-) surface layer is formed, the total film thickness appears to decrease linearly, e.g. etching occurs layer-by-layer being homogenous in depth without hardly any additional surface roughening, see Fig. 2a.

**IV. CONCLUSIONS**

A new method for fast dry etching of inherently textured ZnO using a remote argon - hydrogen plasma has been demonstrated. Unoptimized rates as high as 10 nm s$^{-1}$ have been obtained. Atomic hydrogen is considered to be the reactive species, while the excess of molecular hydrogen in the gas phase does not contribute to the etching. Using in-situ real time spectroscopic ellipsometry (sub-) surface film modification competitive to etching is observed, predominantly in the early stage of plasma exposure at a low substrate temperature.

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APPENDIX A

RESEARCH EQUIPMENT FOR EXPANDING THERMAL PLASMA DEPOSITION
OF TEXTURED ZINC OXIDE
I. INTRODUCTION

The expanding thermal plasma (ETP) is the ultimate remote plasma; in contrast with e.g. electron cyclotron resonance, remote microwave and inductively coupled plasmas, the downstream properties do not influence the plasma source characteristics at all due to the large pressure difference between source and reactor chamber.\(^1\) As opposed to direct plasmas, the substrate holder or electrode does not play a role in plasma production implying the absence of any significant ion bombardment\(^1,2\) and ultraviolet light exposure. The remote configuration of the expanding thermal plasma technique allows separate control of plasma production, gas phase chemistry, and substrate surface treatment,\(^1\) e.g. deposition, etching, facilitating fundamental studies of material properties, plasma processes and film growth.

In order to demonstrate feasibility of the expanding thermal plasma technique for low temperature deposition of textured zinc oxide (ZnO), films are deposited using a commercial pre-production reactor set up which is equipped with a cascaded arc plasma source. In order to facilitate the study of plasma processes and film growth, a new laboratory reactor set up with advanced gas handling system and access for various complementary \textit{in-situ} diagnostics has been designed and constructed. Design criteria include a stable and reproducible liquid precursor feed rate and an accurate substrate temperature control, particularly during plasma exposure.

Here, the expanding thermal plasma technique and research equipment employed for low temperature deposition of textured ZnO will be described in detail.

II. EXPANDING THERMAL PLASMA TECHNIQUE

To characterise the particular cascaded arc plasma source used in this research (a so called low flow cascaded arc)\(^3\), Langmuir probe measurements have been performed. Information about the local ion and electron density and the local electron temperature in an argon plasma is obtained. A double cylindrical

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Typical symmetric double probe I/V characteristic.}
\end{figure}


probe is used, consisting of two tungsten wires with a diameter of 0.25 mm and an exposed length of 5 mm whereas the wires are separated 3 mm. The measurements are performed in radial direction at a distance of 180 mm from the arc outlet, a probe position of 0 mm coincides with the edge and a position of 160 mm with the centre of the reactor chamber. In Fig. 1 a typical double probe I/V characteristic is presented. The probe characteristics obtained are analyzed by the method proposed by Peterson and Talbot. The effective mass of argon ions is equal to 40 amu, it has been assumed no argon ions have been double ionized. Reliable application to expanding thermal plasmas is demonstrated, obtained results are in good agreement with Thomson-Rayleigh scattering measurements.

Fig. 2. (a) Ion density and (b) temperature versus probe position for different arc currents.

The experimental error in density values higher than $1 \cdot 10^{17}$ m$^{-3}$ is less than 5%. The error in the temperature is dependent on the density, for high density values, i.e. $> 5 \cdot 10^{18}$ m$^{-3}$, the absolute error is less than 0.02 eV whereas for low density values, i.e. $1 \cdot 10^{17}$ m$^{-3} < n_e < 5 \cdot 10^{17}$ m$^{-3}$, the absolute error amounts approximately 0.08 eV. For density values lower than $1 \cdot 10^{17}$ m$^{-3}$ the probe becomes inaccurate, the absolute error in the temperature becoming up to 1 eV and the error in the density values of the same order as the density values itself. In Fig. 2 the ion density and temperature versus probe position obtained for fixed
argon flow and different arc currents is shown. Ion densities exceeding $10^{19}$ m$^{-3}$ are obtained. The ion density shows a maximum in the centre of the plasma beam and increases with increasing arc current, as more power is coupled into the plasma. The ionisation efficiency increases quadratically with the arc current. Also the radius of the plasma beam increases with increasing arc current, the increasing ionisation efficiency results in an increase of the ambipolar diffusion coefficient of the ions in the expansion which is driven by the radial gradient in the ion and electron concentration. Note the plasma beam is rather confined, the ion density at the edge of the reactor chamber is low. The temperature shows a maximum value in the centre of the plasma beam and increases with increasing arc current. The low values (< 0.3 eV) indicate a limited dissociative power, electron-induced dissociation or ionisation of any molecular gas added to the argon plasma is unlikely to occur.

For fixed arc current and different argon flows, the highest ion density in the centre of the plasma beam is obtained at the highest argon flow. The ionisation and energy transfer efficiency become higher due to a higher pressure in the cascaded arc cathode housing. However, at a higher arc current a saturation of the ion density occurs with increasing argon flow, the efficiency of energy transfer is independent of the

![Graph](attachment:graph.png)

Fig. 3. (a) Ion density and (b) temperature versus probe position for different reactor chamber pressure.
argon flow. The radius of the plasma beam is independent of the argon flow. The temperature shows a maximum value in the centre of the plasma beam and increases with increasing argon flow. Figure 3 shows the ion density and temperature versus probe position obtained for different reactor chamber pressures for fixed arc current and argon flow. An increasing reactor chamber pressure reduces the ambipolar diffusion coefficient of ions in the expansion resulting in a narrower plasma beam with a higher ion density in the centre. The temperature profile is weakly dependent on the reactor chamber pressure.

III. AIXTRON PRE-PRODUCTION REACTOR SET UP

In order to demonstrate feasibility of the expanding thermal plasma technique for low temperature deposition of textured ZnO, a commercial Aixtron AIX 2300 MX pre-production reactor set up in upside down configuration has been equipped with a cascaded arc plasma source as shown in Fig. 4.

Precursor gases are oxygen (purity grade 5.0), diethyl zinc (DEZ) and additionally for doped films trimethyl aluminum (TMA). Diethyl zinc and trimethyl aluminum were obtained from Aldrich with a purity of 98 respectively 97%. These liquid precursors are supplied to the reactor chamber utilizing conventional Bronkhorst Hi-Tec mass flow controllers and pressure-controlled bubblers using argon (purity grade 5.0) as a carrier gas. Great care was taken to ensure reproducible and quantitative delivery of these precursors.
Employing a bubblizer system, the precursor feed rate depends on the precursor vapour pressure and feed rate of carrier gas passed through the liquid,

\[ F_{\text{precursor}} = \frac{x}{1-x} F_{\text{carrier}} \]  

with \( F_{\text{precursor}} \) the precursor feed rate in sccm, \( F_{\text{carrier}} \) the carrier gas feed rate in sccm and \( x \) the fraction of the precursor vapour pressure over the bubblizer system pressure.

### IV. LABORATORY REACTOR SET UP

In order to facilitate the study of plasma processes and film growth, a new laboratory reactor set up with advanced gas handling system, access for various complementary in-situ diagnostics and a programmable logical control (PLC) unit has been designed and constructed as schematically depicted in Fig. 5. In contrast to its predecessor, the main orientation is horizontal. A loadlock-chamber with magnetic transfer arm is implemented to improve substrate handling.

The gas handling system is shown in Fig. 6, allowing the addition of different precursor gases to the plasma. Here, the liquid precursors are supplied to the reactor chamber utilizing Bronkhorst Hi-Tec Controlled Evaporation and Mixing (CEM) systems. The precursor feed rate is controlled in its natural liquid state at ambient conditions using a liquid mass flow meter and subsequently evaporated in a continuous way with the aid of argon (purity grade 5.0) as a carrier gas. Main features are fast response, high reproducibility, good stability and a low precursor working temperature to prevent possible degradation and/or decomposition.

A sophisticated substrate holder assembly allows for accurate substrate temperature control, additional substrate biasing and substrate replacement via a loadlock-chamber, see Fig. 7. The copper yoke contains four heating elements of 250 W each. Helium flows through the moveable thermally and electrically insulated platform in the centre, providing accurate substrate temperature control by forming a thin heat conducting film between the substrate plate and the substrate.

To validate the actual substrate temperature, interferometry measurements have been performed according to the method proposed by Donnelly and McCaulley\(^9\) sensing small changes in the refractive index and thermal expansion of semiconductor substrates with varying temperature. At an angle of 61° monochromatic light with a wavelength of 1523 nm from a Melles Griot HeNe laser is incident on a double polished crystalline silicon substrate, the reflected light intensity from the substrate is measured using a SiGe detector. The temperature change of the substrate is deduced from the fringes in the detector signal. A similar validation is described in more detail elsewhere.\(^{10}\) In Fig. 8a time dependent interferometry measurement is presented.

A comparison of the temperature applied to the copper yoke and the temperature of a double polished crystalline silicon substrate as deduced from interferometry measurements is shown in Fig. 8b with and without helium backflow. These curves represent the actual temperature of the substrate surface. In absence of helium backflow a negative offset of 50 K is obtained at a copper yoke temperature of 473 K after a heating time of 1200 s, whereas 4 Pa helium backflow reduces the offset to less than 10 K. An increased amount of helium does not reduce the offset further. Besides obtaining the required temperature it is
Fig. 5. ETP laboratory reactor set up. The typical dimensions of the deposition chamber are a length of 800 mm and an inner diameter of 320 mm. The distance between arc outlet and precursor gas injection rings (i.e. oxygen and DEZ / TMA) amounts 65 and 315 mm respectively, the distance between arc outlet and yoke with substrate holder 515 mm. The substrates up to 100x100 mm$^2$ are accurately temperature controlled (423 – 673 K) by a helium backflow and protected from the plasma during ignition by a shutter. During processing the system is pumped using a 500 m$^3$ h$^{-1}$ roots blower allowing for a throttle-valve controlled reactor chamber pressure of 20 – 250 Pa, overnight using a turbo pump reaching a base-pressure of 10$^{-4}$ Pa. A loadlock-chamber with magnetic transfer arm is used to move substrates into the system without venting it.
Fig. 6. ETP laboratory reactor set up gas handling system. Precursor gases are oxygen (purity grade 5.0), DEZ (Aldrich 98% or Akzo Nobel 99.9999%) and additionally for doped films TMA (Aldrich 97% or Akzo Nobel 99.9999%). The liquid precursors are supplied to the reactor chamber utilizing Bronkhorst Hi-Tec CEM systems. Because of the pyrophoric nature of precursors supplied, the vapor is forced to react with oxygen before entering the pump during precursor feed rate stabilization via a bypass line. Spare lines allow for the addition of different precursor gases, e.g. hydrogen with respect to ZnO plasma etching and nitrogen with respect to p-type ZnO deposition.

Fig. 7. ETP laboratory reactor set up substrate holder assembly consisting of copper yoke, moveable platform and substrate plate. The temperature of the copper yoke (up to 673 K) is measured and controlled using a thermocouple connected to a PID-regulator.
essential to maintain this temperature under plasma exposure, i.e. during substrate surface treatment. The observance of an additional fringe in the detector signal under plasma exposure indicates a positive offset of less than 10 K in temperature of the substrate.

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APPENDIX B

VAPOUR PRESSURES OF PRECURSORS FOR EXPANDING THERMAL PLASMA DEPOSITION OF TEXTURED ZINC OXIDE
I. INTRODUCTION

Metal organic compounds are widely used as precursors for chemical vapour deposition processes. Most often these precursors occur in the liquid or solid phase at room temperature and have to be evaporated at elevated temperatures. For accurate control of precursor feed rate, a profound knowledge of the precursor vapor pressure, thermal stability, and purity is required.\textsuperscript{1,3}

Here, vapour pressure measurements are performed using an experimental set up configured in such a way that any disturbing effects resulting from small leaks, partial decomposition of the reactant, volatile contaminants in the precursor or the system itself can be corrected for. The result is an accurate estimate of the true vapour pressure. Vapour pressure measurement curves are determined for diethyl zinc (DEZ) and trimethyl aluminum (TMA), precursors used for the low temperature deposition of textured undoped and aluminum doped ZnO utilizing an expanding thermal argon plasma created by a cascaded arc.\textsuperscript{4}

II. VAPOUR PRESSURE MEASUREMENT SET UP

Diethyl zinc and trimethyl aluminum were obtained from Aldrich with a purity of 98 respectively 97%. Figure 1 shows a schematic representation of the vapor pressure measurement equipment which is described in more detail elsewhere.\textsuperscript{5}

![Diagram](https://via.placeholder.com/150)

Fig. 1. Vapour pressure measurement set up. A fused silica temperature sensor placed near the sample tube allows for an accurate measurement of the precursor temperature, i.e. $\pm 0.05$ K. The measurement equipment is situated in an oven in order to be able to determine vapour pressures at a temperature up to 473 K. The system is pumped using an oil diffusion pump allowing for a base-pressure of 4 Pa.
III. VAPOUR PRESSURE MEASUREMENT PROCEDURE

A typical vapour pressure measurement curve is shown in Fig. 2. The measurements are performed by evacuating compartment 1 and 2. After a short period of pumping, to prevent the loss of precursor, valve 3 is closed (point A in Fig. 2). Valve 3 is opened again after valve 1 and 2 are closed (point B in Fig. 2). The vapour of the precursor subsequently spreads throughout compartment 2 resulting in a sudden increase of pressure difference between the two compartments (point C in Fig. 2). Ideally, the pressure difference should remain constant in time. However, due to any disturbing effects resulting from small leaks, partial decomposition of the reactant, volatile contaminants in the precursor or the system itself the pressure difference might gradually increase in time; extrapolation of the linear part of the vapor pressure curve to the time of the start of the measurement (point D in Fig. 2) will provide the actual vapour pressure without the bias due to small leaks, partial decomposition of the reactant and volatile contaminants.

![Fig. 2. Typical vapour pressure measurement curve.](image)

The presence of volatile contaminants can be corrected for by repeating the measurement several times under the same conditions. The first measurements will contain a contribution of the volatile contaminants, which will decrease in time due to a repeated evacuation. The extrapolated values of the vapor pressure at point D in Fig. 2 will decrease towards a constant value when no volatile contaminants are present anymore. The effect of small leaks and partial decomposition of the reactant into gaseous products can be corrected for by repeating the experiment several times with different time between points A and B in Fig. 2. If small leaks are present or partial decomposition of the reactant occurs in the time between points A and B in Fig. 2, this will result in an increase of the pressure difference beyond point C in Fig. 2. The extrapolated value of the vapour pressure at point D in Fig. 2 provides a corrected vapor pressure exerted by the reactant. A second extrapolation of the obtained values of the corrected vapour pressure at point D in Fig. 2 towards a zero time period results in an accurate value of the true vapour pressure of the examined precursor.
IV. VAPOUR PRESSURE MEASUREMENT CURVES DEZ AND TMA

The vapor pressure measurement curves of diethyl zinc and trimethyl aluminum are shown in Fig. 3 in comparison with literature. No significant decomposition occurred for both precursors in the measured temperature range, presence of volatile contaminants was obviously observed during initial measurements however. Each data set is described by the Clausius-Clapeyron equation,

$$\ln \left( \frac{p}{p_0} \right) = -\frac{\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

with $p$ the vapor pressure in Pa, $p_0$ the vapor pressure at temperature $T_0$, $\Delta H$ the enthalpy of vaporization in kJ mol$^{-1}$ and $R$ the universal gas constant in J mol$^{-1}$ K$^{-1}$.

Fig. 3. Vapour pressure measurement curves of (a) DEZ and (b) TMA in comparison with literature."
Calculated values for the enthalpy of evaporation are summarized in Table 1. In general, lower vapor pressures in comparison to literature are measured. This is characteristic for the employed method; no contribution of volatile contaminants is taken into account. As a result, the corresponding calculated true enthalpies of evaporation are slightly higher.

Table 1. Evaporation enthalpies of DEZ and TMA in comparison to data reported in literature. Error margins are given within at 95% confidence intervals.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>ΔH (kJ mole⁻¹)</th>
<th>ΔH (eV)</th>
<th>Temp. range (K) of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEZ</td>
<td>43.0±0.4</td>
<td>0.445±0.004</td>
<td>273 - 323</td>
</tr>
<tr>
<td>DEZ[6]</td>
<td>40.2</td>
<td>0.416</td>
<td></td>
</tr>
<tr>
<td>DEZ[7]</td>
<td>38.3±0.8</td>
<td>0.397±0.008</td>
<td>251 - 391</td>
</tr>
<tr>
<td>DEZ[8]</td>
<td>38.8±0.4</td>
<td>0.402±0.004</td>
<td></td>
</tr>
<tr>
<td>TMA</td>
<td>41.0±1.5</td>
<td>0.425±0.016</td>
<td>293 - 323</td>
</tr>
<tr>
<td>TMA[6]</td>
<td>41.1</td>
<td>0.426</td>
<td></td>
</tr>
<tr>
<td>TMA[9]</td>
<td>40.8</td>
<td>0.423</td>
<td></td>
</tr>
</tbody>
</table>

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The authors gratefully acknowledge Bas Kniknie and Hans van Hemmen for their contribution to the measurements, and Gerwin Kirchner and Leo Toonen (TNO TPD) for their skilful technical assistance. This research has been financially supported by the Netherlands Agency for Energy and the Environment (NOVEM).

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APPENDIX C

DETECTION OF HYDROXYL SPECIES IN STERILISATION PLASMA USING
CAVITY RING DOWN SPECTROSCOPY

I. INTRODUCTION

Plasma based techniques represent an alternative, safe and versatile route to achieve sterilisation when compared to conventional techniques using autoclaves, irradiation or wet chemicals, especially with respect to the treatment of moisture- and heat sensitive polymer materials. The particular reason for using plasma in sterilisation is the presence of highly reactive species. It is still not clear though whether and how reactive species or photons affect the destruction of microorganisms, yet a rationalisation of processes is required in order to develop more efficient plasma based techniques for sterilisation.

Here, the detection of hydroxyl (OH) species in a hydrogen / oxygen containing 2.45 GHz microwave sterilisation plasma is demonstrated using Cavity Ring Down Spectroscopy (CRDS), a highly sensitive laser-aided diagnostic tool for e.g. plasma phase investigation.

II. EXPERIMENTAL DETAILS

The CRDS set up coupled to the 2.45 GHz microwave sterilisation plasma reactor chamber which is described in detail elsewhere is schematically depicted in Fig. 1. The optical cavity consists of two highly reflective plano-concave mirrors with a radius of curvature of ~ 1000 mm connected to the reactor chamber via bellows that allow for fine-adjustment. The length of the cavity amounts 970 mm. An argon flow protects the mirrors from possible contamination due to the presence of hydrogen. The detection region is situated 70 mm from the microwave source. Depending on the reactor chamber pressure detection occurs in the glow, i.e. in the low pressure regime, or in the immediate afterglow, i.e. in the high pressure regime. A laser pulse (5 ns pulse duration, 10 Hz repetition rate) is produced using a Nd:YAG laser-pumped dye laser (PDL2 Spectra Physics) and sent into the optical cavity.

In the case of OH detection, at the exit of the dye laser operating on sulphorhodamine 640 2 mJ a light pulse around 616 nm is obtained with a bandwidth of 0.28 cm\(^{-1}\) which is frequency doubled with a potassium deutero phosphate crystal to generate UV light. The light leaking out of the cavity passes through
a narrow band filter cutting the background light from the plasma and is detected by a photomultiplier tube (Hamamatsu R928), which is connected to an oscilloscope (Tektronix TDS 340A, 500 Ms s$^{-1}$ sampling rate). A LabView program controls the wavelength stepping of the dye laser and reads the recorded transients via a GPIB interface. At every wavelength typically 64 transients are averaged. The averaged transient is subsequently fitted with a standard least-squares fitting routine to an exponentially decaying function resulting in the characteristic ring down time. Comparing the ring down time for the optical cavity in presence of absorbing species with the ring down for the empty optical cavity provides the absorption of species present. For an empty optical cavity a ring down time of approximately 400 ns is recorded from which a mirror reflectivity of 0.992 at 308 nm is deduced.

III. RESULTS AND DISCUSSION

The OH spectrum has been investigated within the $A^2\Sigma^{-} (\nu = 0) \leftarrow X^2\Pi (\nu' = 0)$ band. Two regions were monitored, the $I_0$ lines (306.495 nm and 306.510 nm) belonging to the $G_0$ group and the $I_2$ lines

![Fig. 2. The $G_0$ (a) and $G_2$ (b) group of the OH spectrum within the $A^2\Sigma^{-} (\nu = 0) \leftarrow X^2\Pi (\nu' = 0)$ band.](image-url)
Fig. 3. The OH absorption per pass on the I₀₂ transitions of the $\text{A}^2\Sigma^+ (\nu = 0) \leftarrow \text{X}^2\Pi (\nu = 0)$ band versus microwave power for two different values of reactor chamber pressure. (308.154 nm, 308.162 nm and 308.166 nm) belonging to the $G_2$ group as shown in Fig. 2.

The line-integrated OH absorption per pass versus microwave power and reactor chamber pressure is shown in Fig. 3 and 4. The OH absorption, i.e. formation, increases with the microwave power as molecular dissociation becomes more efficient. With increasing reactor chamber pressure the absorption decreases, most probably due to the fact that the discharge becomes more confined, i.e. the detection occurs not in the glow but in the immediate afterglow. The experimental error amounts $5 \times 10^{-6}$ for the absorption per pass in the $G_0$ group and $1 \times 10^{-6}$ for the absorption per pass in the $G_2$ group. Figure 4 shows the good agreement between the data series recorded in the two different OH absorption regions.

Fig. 4. The line-integrated OH absorption per pass on the I₀₁ and I₂₃ transitions of the $\text{A}^2\Sigma^\prime (\nu = 0) \leftarrow \text{X}^2\Pi (\nu = 0)$ band versus microwave power.
In Fig. 5 the line-integrated OH absorption per pass versus the ratio of precursor gases hydrogen to oxygen is shown. The OH formation, appears to be high at a low ratio of hydrogen to oxygen, which is indicative for a high dissociation efficiency of hydrogen compared to oxygen. Again, a good agreement between the data series recorded in the two different OH absorption regions is observed.

![Fig. 5. The line-integrated OH absorption per pass on the I0\(^2\) and I2\(^3\) transitions of the A\(^2\)\(\Sigma^+\)(\(\nu = 0\)) \(\leftrightarrow\) X\(^2\)\(\Pi\)(\(\nu' = 0\)) band versus hydrogen to oxygen ratio.](image)

From the ratio of the line-integrated absorption per pass recorded in the two different OH absorption regions the rotational temperature of the OH species is determined. The program LIFBASE\(^{10}\) was used to simulate the OH absorption in the two spectral regions, yielding a rotational temperature ± 150 K which increases with microwave power as shown in Fig. 6. The OH absorption spectrum can serve as a molecular pyrometer.\(^{11,12}\)

![Fig. 6. The OH rotational temperature versus microwave power obtained from the simulated ratio of line-integrated absorption per pass on the I0\(^2\) and I2\(^3\) transitions of the A\(^2\)\(\Sigma^+\)(\(\nu = 0\)) \(\leftrightarrow\) X\(^2\)\(\Pi\)(\(\nu' = 0\)) band.](image)
IV. CONCLUSIONS

The detection of hydroxyl (OH) species in a hydrogen / oxygen containing 2.45 GHz microwave sterilisation plasma is demonstrated using Cavity Ring Down Spectroscopy (CRDS). The OH spectrum has been investigated within the $A^2\Sigma^+ (\nu = 0) \leftrightarrow X^2\Pi (\nu' = 0)$ band. Two regions were monitored, the $I_0$ lines (306.495 nm and 306.510 nm) belonging to the $G_0$ group and the $I_2$ lines (308.154 nm, 308.162 nm and 308.166 nm) belonging to the $G_2$ group. The OH absorption, i.e. formation, increases with the microwave power as molecular dissociation becomes more efficient. With increasing reactor chamber pressure the absorption decreases, most probably due to the fact that the discharge becomes more confined, i.e. the detection occurs not in the glow but in the immediate afterglow. The OH formation appears to be high at a low ratio of hydrogen to oxygen, which is indicative for a high dissociation efficiency of hydrogen compared to oxygen. A good agreement between the data series recorded in the two different OH absorption regions is observed. The rotational temperature of the OH species, in general close to the gas temperature, is determined.

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Simultaneously possessing transparency in the visible region, close to that of insulators, and electrical conductivity, close to that of metals, transparent conducting oxide (TCO) thin films form a highly attractive class of materials for a wide variety of applications like thin film solar cells, architectural glazing, flat panel displays, electro chromic devices, surface acoustic wave devices and gas sensors. Each application however sets different demands on the materials properties. An appropriate measure of the performance of a transparent conducting oxide reflecting its intrinsic, i.e. bulk, quality is the ratio of the electrical conductivity $\sigma$ to the visible absorption coefficient $\alpha$. The quantity $\sigma/\alpha$ is a Figure of Merit (FM) for rating transparent conducting oxides, the larger the value of this quantity the better the performance of the transparent conducting oxide. Besides intrinsic quality, generally also specific extrinsic quality is required like, e.g., mechanical, chemical and thermal durability, surface morphology, and etchability. Deposition temperature, cost and environmental impact are other factors that may influence the choice of transparent conducting oxide for any particular application.

A transparent conducting oxide of emerging technological interest is zinc oxide (ZnO) challenging the development of sophisticated synthesis technologies to allow for highly tailorable material properties and consequently to raise the prospect of a wide variety of applications. The goal of this thesis is to design and develop a process for low temperature deposition of textured zinc oxide films using expanding thermal plasma (ETP). As an example, suitability for application as a front contact in thin film solar cells is discussed. The expanding thermal plasma is the ultimate remote plasma; in contrast with e.g. electron cyclotron resonance, remote microwave and inductively coupled plasmas, the downstream properties do not influence the plasma source characteristics at all due to the large pressure difference between cascaded arc plasma source and reactor chamber. As opposed to direct plasmas, the substrate holder or electrode does not play a role in plasma production implying the absence of any significant ion bombardment and ultraviolet light exposure. The remote configuration of the expanding thermal plasma technique allows separate control of plasma production, gas phase chemistry, and substrate surface treatment, e.g. deposition, etching, facilitating fundamental studies of material properties, plasma processes and film growth.

Demonstration of low temperature textured zinc oxide deposition from oxygen, diethyl zinc and additionally for doped films trimethyl aluminum utilizing the expanding thermal plasma technique is discussed. Property control is demonstrated, the remote configuration of the expanding thermal plasma technique allows for separate adjustment of plasma production (e.g. arc argon flow), gas phase chemistry (e.g. oxygen flow, trimethyl aluminum flow) and near-substrate conditions (e.g. reactor chamber pressure, temperature), independently affecting intrinsic, i.e. bulk, and application dependent relevant extrinsic transparent conducting oxide quality. Control of film composition is mainly governed by plasma production and gas phase chemistry inherently inducing a significant contribution of film morphology, whereas control of film morphology solely is governed by near-substrate conditions. Especially ratio of zinc to oxygen and
reactor chamber pressure appear to be determinative in obtaining zinc oxide exhibiting the appropriate intrinsic and extrinsic quality for application in thin film solar cells, i.e. a high electrical conductivity, a high visible transmittance, a textured rough surface morphology and a strong hydrogen plasma resistance.

The suitability for application of expanding thermal plasma deposited zinc oxide in thin film amorphous silicon pin solar cells is demonstrated, the solar cell performance of appropriate undoped and aluminium doped zinc oxide is comparable with respect to state-of-the-art Asahi U-type fluorine-doped tin oxide. A high spectral response has been obtained in the long wavelength regime indicating an effective light trapping due to optical scattering at the rough zinc oxide / amorphous silicon interface.

Plasma processes and film growth of expanding thermal plasma deposited textured zinc oxide is discussed. The chemical reactivity is characterized by the argon ion and electron flux emanating from the cascaded arc plasma source. In all conditions explored an excess of argon ions and low temperature electrons which represent the chemistry taking place is available, i.e. the plasma is underloaded with precursor gases. The plasma induced decomposition mechanism involves charge exchange with argon ions and consecutive dissociative recombination with electrons emanating from the cascaded arc plasma source. The presence of reactive atomic species, i.e. Zn* (transition $4p^3P_2 \rightarrow 5s^3S_1$, 481 nm) and O* (transition $3s^3S_1 \rightarrow 3p^5P_{0,1,2}$, 777 nm), is confirmed with optical emission spectroscopy measurements. In addition a strong signal representing H* (transition Balmer-$\alpha$, 656 nm) is present. Atomic as well as molecular oxygen might directly attribute to the decomposition of diethyl zinc and formation of different bond states, i.e. Zn-O, although it is suggested that in the gas phase oxygen will mainly affect the hydrocarbon chemistry. The plasma chemistry, i.e. the behavior of atomic oxygen and zinc, is reported to be very similar to combustion chemistry. The absence of significant amount of residual carbon in the films favors a mechanism involving the dissociation of the Zn-C bonds in the plasma instead of at the surface. Film growth is suggested to proceed by the adsorption of particular zinc species followed by subsequent reaction with oxygen, the deposition rate is directly proportional to the arrival rate of the particular reactive species. Best intrinsic transparent conducting oxide quality, i.e. film conductivity, is obtained at highest deposition rate. Besides the ratio and nature of particular reactive species arriving at the substrate surface, an important issue to be considered during surface texture growth is the surface mobility of species arriving at the substrate surface. It is believed that particular zinc species adsorb on the surface in a weakly bounded highly mobile state.

With respect to surface texturing inherently obtained during deposition, it is suggested that film growth might be the interplay of deposition and etching. Hydrogen species might contribute in the surface texturing, fast dry etching of zinc oxide is demonstrated utilizing a remote argon – hydrogen plasma. (Sub-)surface film modification competitive to etching is observed, predominantly in the early stage of plasma exposure at a low substrate temperature.
SAMENVATTING

Het verenigen van transparantie in het zichtbare gebied, vergelijkbaar met isolatoren, en elektrische geleidbaarheid, vergelijkbaar met metalen, maakt transparant geleidend oxide (TCO) dunne films een aantrekkelijke klasse van materialen voor een breed toepassingsgebied zoals dunne film zonnecellen, architecturale verglazing, flat panel displays, electrochrome systemen, surface acoustic wave devices en gassensoren. Echter, elke individuele toepassing stelt specifieke eisen aan de materiaaleigenschappen. Een maat voor de performantie van een transparant geleidend oxide die de intrinsieke, d.w.z. bulk, eigenschappen weerspiegelt, is de verhouding van elektrische geleidbaarheid $\sigma$ en zichtbare absorptie coëfficiënt $\alpha$. De parameter $\sigma/\alpha$ is een Figure of Merit (FM) voor het beoordelen van transparant geleidbare oxides, hoe groter de waarde van deze parameter des te beter de performantie van het transparant geleidend oxide. Naast intrinsieke kwaliteit is in het algemeen ook een specifieke extrinsieke kwaliteit vereist, zoals bijvoorbeeld mechanische, chemische en thermische duurzaamheid, oppervlaktemorfologie en etsbaarheid. Depositematig, kosten van productie en invloed op de leefomgeving vormen andere factoren die de keuze van een transparant geleidend oxide voor een specifieke toepassing kunnen beïnvloeden.

Een transparent geleidend oxide van opkomend technologisch belang is zinkoxide. Zinkoxide vormt een uitdaging voor de ontwikkeling van geavanceerde synthesetechnologieën die een vergaande gerichte beïnvloeding van materiaaleigenschappen en bijgevolg het perspectief op een grote verscheidenheid aan toepassingen toestaan. Het doel van dit proefschrift is het ontwerpen en ontwikkelen van een proces voor lage temperatuur depositie van getextureerde zinkoxide films gebruik makende van een expanderend thermisch plasma (ETP). Als een voorbeeld wordt de toepasbaarheid van dergelijk materiaal in dunne film zonnecellen onderzocht. Een expanderend thermisch plasma is het ultieme remote plasma; in tegenstelling tot bijvoorbeeld elektron cyclotron resonantie, remote microgolf en inductief gekoppelde plasmas, beïnvloeden de downstream eigenschappen in het geheel niet de plasma bron karakteristiek vanwege het grote drukverschil tussen casacadeboog plasmabron en reactorkamer. In tegenstelling tot directe plasma’s speelt de substraathouder of electrode geen rol in de plasma productie hetgeen de afwezigheid van enig significant ionen bombardement en ultraviolet straling inhoudt. De remote configuratie van de expanderend thermisch plasma techniek staat een afzonderlijke beïnvloeding en controle toe van plasmaproductie, gasfasechemie en substraat oppervlaktebehandeling, bv. depositie, etsen, hetgeen een fundamentele studie van materiaaleigenschappen, plasmaprocessen en film aangroei vereenvoudigt.

Demonstratie van lage temperatuur depositie van getextureerd zinkoxide uitgaande van zuurstof, diethyllzink en voor gedoteerde films trimethylaluminium gebruik makende van de expanderend thermisch plasma techniek is beschreven. Controle van materiaal eigenschappen is gedemonstreerd, de remote configuratie van de expanderend thermisch plasma techniek staat een afzonderlijke beïnvloeding toe van plasmaproductie (bv. argon flux door de plasma bron), gasfasechemie (bv. zuurstof flux, trimethyl aluminium flux) en condities in de nabijheid van het substraat (bv. reactorkamer druk, temperatuur),
resulterend in een onafhankelijke controle van intrinsieke, d.w.z. bulk, en toepassingsafhankelijke relevante extrinsieke transparant geleidend oxide kwaliteit. Controle van film samenstelling wordt voornamelijk bewerkstelligd door plasmaproductie en gasfasechemie welke inherent tevens een significante invloed uitoefenen op filmmorphologie, terwijl controle van filmmorphologie afzonderlijk voornamelijk wordt bewerkstelligd door condities in de nabijheid van het substraat. Met name de verhouding zink tot zuurstof en de reactorkamer druk blijken bepalend voor het verkrijgen van zink oxide met de gewenste intrinsieke en extrinsieke kwaliteit voor toepassing in dunne film zonnecellen, d.w.z. een hoge elektrische geleidbaarheid, een hoge transparantheid in het zichtbare golfentge gebied, een getextureerde ruwe oppervlaktemorfologie en een sterke resistentie tegen waterstofplasma.

De toepasbaarheid van expanderend thermisch plasma gedeponeerd zinkoxide in dunne film amorf silicium pin zonnecellen is gedenomstreerd, de performatie van cellen gebruik makende van geschild ongedoerte en aluminium gedoteerde zinkoxide is vergelijkbaar met state-of-the-art Asahi U-type fluor gedopeerd tinoxide. Een hoge spectrale respons in het lange golflengte gebied is indicatief voor een effectieve lichtopsluiting ten gevolge van verstrooïng aan het ruwe zinkoxide / amorf silicium grensvlak.

Plasmaprocessen en film aangroei van expanderend thermisch plasma gedeponeerd getextureerd zinkoxide zijn bediscussieerd. De chemische reactiviteit wordt uitsluitend gekarakteriseerd door de argon ionen en elektronen flux die de cascadeboog plasmabron verlaat. In het bereik van geëxplorereerde procescondities is een overmaat argon ionen en lage temperatuur elektronen aanwezig die de opdripping chemie representeren, d.w.z. het plasma is onderladen met precursor gassen. De aanwezigheid van reactieve atomaire deeltjes, d.w.z. Zn* (transitie 4pP312 ← 5sS1, 481 nm) en O* (transitie 3sS1 ← 3pP0,1,2, 777 nm) is bevestigd met optische emissie spectroscopie metingen. Tevens is een sterk signaal representatief voor H* (transitie Balmer-α, 656 nm) aanwezig. Zowel atomaal als moleculair zuurstof kan direct bijdragen aan de decompositie van diethyl zink en de vorming van verschillende bindingstoestanden, d.w.z. Zn-O. Het wordt echter voorgesteld dat zuurstof in de gasfase hoofdzakelijk van invloed is op de koolwaterstofchemie. De plasmachemie, d.w.z. het gedrag van atomaar zuurstof en zink, is zeer gelijkvormig aan verbrandingschemie. De afwezigheid van een significante hoeveelheid overblijvend koolstof in de films geeft de voorkeur aan een mechanisme waarbij dissociatie van de Zn-C bindingen plaatsvindt in het plasma in plaats van aan het oppervlak. Film aangroei wordt voorgesteld plaats te vinden middels adsorptie van bepaalde zink bevattende deeltjes gevolgd door reactie met zuurstof, de depositie snelheid is direct evenredig met de aankomst snelheid van de reactieve deeltjes. Opmerkelijk genoeg wordt de beste intrinsieke transparant geleidend oxide kwaliteit, d.w.z. geleiding van de film, verkregen bij de hoogste depositiesnelheid. Naast de verhouding en aard van de reactieve deeltjes die bij het substraatoppervlak aankomen, is het gedurende oppervlakte getextureerde aangroei van belang de oppervlakte mobiliteit van deze deeltjes in opsomschuw te nemen. Het wordt aangenomen dat bepaalde zinkdeeltjes aan het oppervlak adsorberen in een zwak gebonden zeer mobiele toestand.

Met betrekking tot oppervlakte texturering inherent verkregen gedurende depositie, wordt voorgesteld dat film groei een samenspel is van depositie en etsen. Waterstofdeeltjes kunnen bijdragen aan de oppervlakte texturering, hoge snelheid droogsetten van zinkoxide gebruikt makende van een remote argon-waterstof plasma is gedenomstreerd. Oppervlakte filmmodificatie concurrerend aan etsen is waargenomen en hoofdzakelijk aanwezig in het initiele stadium van plasma blootstelling bij een lage substraat temperatuur.
PUBLICATIONS RELATED TO THIS WORK

JOURNAL PUBLICATIONS


R. Groenen, J. Löffler, J.L. Linden, R.E.I. Schropp, M.C.M. van de Sanden, Property control of expanding thermal plasma deposited textured zinc oxide with focus on thin film solar cell applications, Thin Solid Films, accepted for publication.

R. Groenen, J.L. Linden, M.C.M. van de Sanden, Plasma processes and film growth of expanding thermal plasma deposited textured zinc oxide, Plasma Processes Polym., accepted for publication.

PROCEEDINGS OF INTERNATIONAL CONFERENCES


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CURRICULUM VITAE

23 July 1974
Born in Eindhoven, The Netherlands

September 1986
Student Gymnasium, Augustinianum, Eindhoven

September 1992
MSc student Chemical Engineering, Eindhoven University of Technology
Industrial traineeship Philips CFT, Eindhoven

February 1999
PhD student Applied Physics, Eindhoven University of Technology
Working visit Institute for Health and Consumer Protection, Joint Research Centre, Ispra, Italy

February 2004
R&D Project Manager Vacuum Technology, NV Bekaert SA, Belgium