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Interaction between \( \text{O}_2 \) and \( \text{ZnO} \) films probed by time-dependent second-harmonic generation

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The interaction between \( \text{O}_2 \) and \( \text{ZnO} \) thin films prepared by atomic layer deposition has been investigated by time-dependent second-harmonic generation, by probing the electric field induced by adsorbed oxygen molecules on the surface. The second-harmonic generated signal decays upon laser exposure due to two-photon assisted desorption of \( \text{O}_2 \). Blocking and unblocking the laser beam for different time intervals reveals the adsorption rate of \( \text{O}_2 \) onto \( \text{ZnO} \). The results demonstrate that electric field induced second-harmonic generation provides a versatile non-contact probe of the adsorption kinetics of molecules on \( \text{ZnO} \) thin films. © 2014 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4863942]

Oxygen interaction with \( \text{ZnO} \) thin films and nanowires has been intensively studied due to the interesting applications of \( \text{ZnO} \) such as in \( \text{O}_2 \) sensors1,2 and UV detectors.3,4 \( \text{O}_2 \) can adsorb at surface defect sites by capturing a free electron from the \( n \)-type \( \text{ZnO} \) thin film,5 resulting in \( \text{O}_2 \) formation at the surface. The associated electric field leads to upward bending of the energy bands of \( \text{ZnO} \) and a depletion region is created.1–8 Therefore, the free electrons are repelled from the surface, and a corresponding increase of surface resistivity can be observed.1,3,9 Exposing the film to UV photons with an energy larger than the band gap of 3.4 eV generates electron–hole pairs. The holes will migrate along the potential slope created by the band bending and recombine with the oxygen ions located at the surface. This process causes photo desorption of \( \text{O}_2 \) and a decrease in resistivity is observed, hence making it possible to use the system as an UV detector and \( \text{O}_2 \) sensor.

Optical second-harmonic generation (SHG) is a well-established tool for investigations of adsorption of species on surfaces.10 The technique has been used for studies of adsorption and desorption of species at defect sites on rutile \( \text{TiO}_2 \) surfaces. Shultz et al.11 have investigated UV defect generation and subsequent time dependent healing of the defects by \( \text{O}_2 \) exposure. Also, the interaction of \( \text{TiO}_2 \) with water has been probed by SHG.12 In these investigations, the sensitivity of SHG to adsorbed molecules has been ascribed to a general sensitivity to defects through their modifications of the surface band structure. However, a number of investigations have demonstrated a strong sensitivity of SHG to charges at semiconductor surfaces and interfaces through an electric field induced third-order effect. Important information about the space-charge regions at interfaces between silicon and thin films has been revealed.13–15 Intensive research has been carried out on the dynamics of electric field induced SHG (EFISH) from adsorption of \( \text{O}_2 \) ions on native oxide covered silicon surfaces.16,17

In this Letter, we demonstrate that the dynamics of adsorption and desorption of \( \text{O}_2 \) on \( \text{ZnO} \) thin films can be probed by time-dependent second-harmonic generation (TD-SHG). The oxygen-induced field at the surface of the \( \text{ZnO} \) leads to an EFISH contribution. At the same time, the probing laser beam can lead to desorption of adsorbed oxygen and hence cause a decrease in the SHG response. By blocking and unblocking the laser beam, the decay and recovery of the signal due to desorption and adsorption of oxygen can be studied. It was found that the adsorption rates estimated by TD-SHG are comparable to those determined by resistivity measurements.

Thin (20 nm) polycrystalline \( \text{ZnO} \) films were deposited by atomic layer deposition (ALD) at 200 ºC (labeled T200) and at 180 ºC (labeled T180) in an Oxford Instruments OpAL reactor, using \( \text{H}_2 \text{O} \) as the oxidant and \( (\text{C}_2\text{H}_3)_2\text{Zn} \) as the metal precursor. The thin films were deposited on \( n \)-type Si(100) wafers with native oxide. Additionally, a sample prepared at 200 ºC was capped directly after the deposition with a 5 nm thick \( \text{Al}_2\text{O}_3 \) by ALD, from trimethylaluminum (TMA, \( \text{Al}_3\text{(CH}_3)_3 \)) and \( \text{H}_2\text{O} \). Furthermore, a 86 nm thick \( \text{ZnO} \) film was deposited on Corning 7059 glass. More details on the preparation and properties of the \( \text{ZnO} \) films can be found elsewhere.6 The linear optical properties and thickness of the different thin films were determined with spectroscopy ellipsometry (SE) measurements (J. A. Woollam, Inc., M2000U (0.75–5.0 eV)).

The TD-SHG experiments were performed in reflection mode using a mode-locked Ti:Sapphire laser (Tsunami, Spectra-Physics) delivering 90 fs p-polarized pulses (80 MHz repetition rate) with a photon energy of 1.675 eV focused onto the sample with a doublet lens (focal length 200 mm) resulting in an average laser intensity varying from 10 to 50 MW/cm². Colored glass filters (Schott BG40) were used to separate the excitation radiation from the second-harmonic (SH) radiation. The SHG signal was

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detected with a photomultiplier tube coupled to single photon counting electronics. The angle of incidence of the laser beam was 30° except for the measurements in which the surrounding ambient of the sample was changed by using a closed chamber. In these experiments, the sample was placed at 45° angle of incidence. The chamber could be purged with dry nitrogen, and air could be reintroduced through a valve. All the measurements were performed at room temperature and a relative humidity of 40%. Moreover, T200 was exposed to 3 mW/cm² radiation at 237 nm from a Cole-Parmer Pen-Ray UV lamp (YO-97606-00).

It is noted that both single crystalline and polycrystalline ZnO show a bulk second-harmonic response, due to its hexagonal closed packed structure. The 6 mm symmetry allows three second-order tensor elements to contribute to a bulk SHG signal.

Figure 1 shows a typical TD-SHG signal (blue dots) from T200. The rapid decrease of signal upon laser exposure can be attributed to photon-assisted O₂ desorption. After the measured SH decay, the entire sample was exposed to UV irradiation for 15 min, thereby removing O₂ located at the surface of the sample. Recording of SHG was started again 1 min after the UV illumination (green squares) at a different spot to rule out the influence of the probing laser. Only a very small decrease in the SH signal is seen compared to the first measured decay. The small decay is most likely related to O₂ absorbed at the ZnO surface during the 1 min time interval between UV exposure and the SHG experiment. An overall increase in signal after the UV illumination is noted (Fig. 1). Under UV illumination in an atmosphere containing water, Feng et al. showed that it is energetically more favorable to adsorb hydroxyl groups (OH⁻) on the ZnO surface defect sites instead of oxygen. Additionally, Li et al. and Ahn et al. found a slow increase in resistivity upon UV illumination due to OH⁻ adsorption on defect sites. Thus, OH⁻ located at the surface cause an upward bending of the energy bands leading to a larger SHG response, as can be seen in Fig. 1.

The red curve is the TD-SHG signal from the Al₂O₃ capped ZnO film. Since the reflectivity of Al₂O₃ is different from that of ZnO, the SH signal amplitude is multiplied by a factor of 1.37 to correct for this linear optical effect (the value is derived from SE results). Note that the TD-SHG signal is constant in time since ZnO no longer is in contact with O₂, while the corrected signal amplitude is approximately the same as for T200. Furthermore, decay curves have also been measured for the 86 nm thick ZnO film prepared on a glass substrate. These observations demonstrate that the TD-SHG signals are related to the interaction between O₂ and the surface of the ZnO thin films, rather than to the silicon substrate.

Fig. 2(a) shows a typical TD-SHG signal from T180 along with a fit based on an exponential decay of the SHG signal of the form

\[
I_{2\omega}(t) = \left[ a_{\text{bulk}} + b_{O_2} e^{(-t/\tau_{\text{de}})} \right]^2.
\]

This equation represents a coherent addition of the nonlinear optical response of a film without adsorbed oxygen \(a_{\text{bulk}}\) and an oxygen-induced response of amplitude \(b_{O_2}\) decaying with a desorption time constant \(\tau_{\text{de}}\) under laser illumination. As mentioned above, a polycrystalline ZnO film has a bulk SHG response. Further evidence for the bulk character of the \(a_{\text{bulk}}\) term comes from its magnitude which is several orders of magnitude larger than the response from the Si substrate. The SHG signal from the oxygen-induced E-field \(E_{dc}\), \(O_2\), is related to the effective bulk third-order response tensor \(\chi^{(3)}\) through \(E_{2\omega} = \chi^{(3)} E_{dc} E_{dc}\), where \(E_{dc}\) is related to the band bending in the depletion region generated by the adsorbed oxygen ions.

Figure 2(b) illustrates, on a double logarithmic scale, the behavior of the time constant \(\tau_{\text{de}}\) as a function of the average laser power. The time constant decreases with average laser power and can be described by \(1/\tau_{\text{de}} \propto P^{1.5\pm0.1}\), indicating that a multi-photon process play a role in the desorption rather than thermal desorption. Additional evidence stems from SHG experiments carried out with an excitation...
photon energy of 1.55 eV, where no detectable decay of the SHG signal was observed. With 1.55 eV photons, the two-photon energy is too low to excite electrons across the band gap of ZnO, hence, no photo desorption can occur. This indicates that a two-photon process is responsible for O₂ desorption with 1.675 eV excitation energy. Thus, the laser beam generating the SHG probe signal is also responsible for the decay of the EFISH signal.

Investigations of the adsorption dynamics of O₂ are done by blocking the laser for different time intervals, so-called dark times \( t_d \), followed by unblocking the beam to monitor the light-induced decay of SHG. Figure 3(a) shows a measurement on a fixed spot on T180 in ambient air, where the dark times are varied from 1 to 16 min. The level of the recovered signal \( \Delta I_{2\omega} \) increases with the dark time. When the same experiments are performed in N₂ environment, the signal amplitude never recovers, see Fig. 3(b). Additionally, when the sample was re-exposed to ambient air, the decay curve reappeared, see Fig. 3(c).

Recovery of the SHG signal from O₂ adsorption can be represented by \( \Delta I_{2\omega} \), the change in SHG signal normalized to \( \Delta I_{2\omega}^0 \), the change in SHG signal from the first measured decay curve, see Fig. 3. The results are plotted in Fig. 4 as a function of dark time. The red squares in Fig. 4 are the data points extracted from Fig. 3(a) and the blue triangles are from Fig. 3(c).

Lampe and Müller showed in their analysis of adsorption-induced changes in resistivity that the adsorption of oxygen ions on ZnO follows a logarithmic increase with O₂ exposure time. In addition, Barry and Stone corroborated this behavior through pressure dependent measurements. In order to relate this to the TD-SHG results, it is noted that the total charge \( Q \) from adsorbed \( O_2^- \) is balanced by the charge in the depletion region. This can be approximated by \( Q = wN_d j \), where \( N_d \) is the doping density and \( w \) is the width of the depletion region. In a first approximation, the oxygen-induced E-field, \( E_{dc} \), will be proportional to \( w \). Therefore, the recovery of the SHG signal as a function of dark time \( \Delta I_{2\omega}(t_d) \), which is proportional to \( (E_{dc})^2 \), can be represented by the square of the logarithmic change in adsorbed \( O_2^- \) as presented by Barry and Stone in the form

\[
\frac{\Delta I_{2\omega}(t_d)}{\Delta I_{2\omega}^0} \propto A \left[ \ln \left( t_d + \frac{1}{\tau_{ad}} \right) + \ln(\tau_{ad}) \right]^2.
\]  

Here, \( A \) is related to the density of available surface defect sites and \( \tau_{ad} \) is a characteristic time constant for adsorption on these sites. Using this relationship, the data in Fig. 4 can be fitted and provide the rate of adsorption \( \tau_{ad} \) of O₂. For experiments in ambient air before and after the N₂ purge measurements, the adsorption rates were estimated to be \( \tau_{ad} = 2.6 \pm 0.7 s \) and \( \tau_{ad} = 2.1 \pm 0.7 s \), respectively. The estimated TD-SHG adsorption rates compare fairly well to adsorption rates determined with resistivity measurement on a ZnO film, \( \tau_{ad} = 1 s \) at 280 °C (see Ref. 1) and nanowires at room temperature \( \tau_{ad} = 4.6s \) (see Ref. 22) and \( \tau_{ad} = 1.3s \) (see Ref. 3). Additionally, Barry and Stone measured the adsorption rate to \( \tau_{ad} = 3.5 s \) from a ZnO powder sample at room temperature.

The faster O₂ response time \( \tau_{ad} \) of T180 after the N₂ experiment could be related to the fact that N₂ purging also removes physisorbed H₂O from the surface, leaving behind more defect sites that can adsorb O₂. Hence, the factor \( A \) in Eq. (2) has changed. Moreover, Li et al. found a significant dependence of \( \tau_{ad} \) on the amount of H₂O present in the atmosphere which is still not fully understood. Interestingly, an overall increase in base amplitude is noted when T180 is re-exposed to ambient air, see Fig. 3(c). This amplitude increase can be fitted with Eq. (2) indicating an adsorption process. Hence, it may be related to OH⁻ forming on defect sites due to the probing laser. Alternatively, this overall increase could be independent on the probing laser since water vapor in the ambient air has previously been shown to affect the dynamics of the ZnO-O₂ system. Isolated physisorbed water molecules remain undissociated on the
surface and do not capture electrons or holes. However, molecules adsorbed at neighboring surface sites may dissociate and enable oxygen atoms to capture electrons from the ZnO surface\textsuperscript{21,24} leading to an increased EFISH for high density of H\textsubscript{2}O molecules on the ZnO surface.

Finally, we would like to address the difference in the SHG signal amplitudes between the measurement in Fig. 1 ($\Delta I_{2\omega} = 1.6$, T200) and Fig. 2 ($\Delta I_{2\omega} = 2.7$, T180). T180 was prepared at a slightly lower substrate temperature (180 $\degree$C)\textsuperscript{14} resulting in smaller grain sizes, as seen in the two AFM images in Figs. 2(c) and 2(d). Hence, more defect sites are expected to be present for T180 leading to a stronger oxygen induced electric field from more adsorbed O\textsuperscript{2-} ions. This indicates that the amplitude change of the TD-SHG signal can be related to the surface morphology of the ZnO thin films.

In conclusion, time-dependent second-harmonic generation curves recorded from ZnO thin films deposited by ALD can be correlated to desorption/adsorption of O\textsubscript{2} on surface defect sites. A two-photon absorption process was found to be responsible for the laser-induced photo desorption of O\textsubscript{2}. Adsorption rates for O\textsubscript{2} estimated by TD-SHG were found to be comparable to rates determined through resistivity measurements. TD-SHG can thus be used to investigate the interaction between O\textsubscript{2} and ZnO surface defect sites, and the technique may be extended to study adsorption kinetics of other species on ZnO thin films.

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