Light-induced reversible optical properties of hydrogenated amorphous silicon

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Light-Induced Reversible Optical Properties of Hydrogenated Amorphous Silicon: A Promising Optically Programmable Photonic Material

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Reversible optical properties (refractive index, \( n \), and extinction coefficient, \( k \)) upon light soaking and annealing are predicted to originate from the metastable properties of hydrogenated amorphous silicon (a-Si:H). Optically programmable photonic devices can be demonstrated when a-Si:H is established as a potential programmable photonic material. Therefore, the effects of prolonged high intensity light soaking and annealing are investigated. A set of a-Si:H films is deposited by inductively coupled plasma-enhanced chemical vapor deposition (ICP-PECVD) near the amorphous/nano-crystalline phase transition that have significantly different hydrogen content and microstructures. Spectroscopic ellipsometry shows that the imaginary part of the pseudo dielectric function \(<\varepsilon_2>\) values near the peak clearly decreases after light soaking and this decrease can be reversed after annealing. No loss of Si-bonded hydrogen is observed after repeated cycles of light soaking and annealing and an inverse correlation between this reversibility and the hydrogen content is found. A change in the bulk optical properties is likely the main contributor to the observed metastable effect, suggesting a reversible refractive index change. Repeated cycles of reversible \(<\varepsilon_2>\) behavior are demonstrated which together with the magnitude of reversibility (as high as 3.7% at 3.6 eV) illustrates the potential of a-Si:H for future programmable photonic devices.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) and its alloys have a long history of research with respect to commercial applications, such as thin-film transistors for liquid crystal displays, thin-film silicon solar cells,[3] and wafer-based silicon heterojunction solar cells.[2] Recently, a-Si:H has been receiving a renewed research interest from the optoelectronics and photonics communities. Defect-related optical absorption in the infrared range makes the performance of a-Si:H photons inferior to the traditional silicon photonics.[1] Despite this fact, key advantages like favorable and low-cost deposition on potentially any substrate, tunable refractive index based on the deposition chemistry, good compatibility with CMOS back-end optoelectronics interconnect, and high optical non-linearity render a-Si:H an attractive material choice for photonics.[4–7] Additionally, we demonstrate here a unique property of a-Si:H that can be valuable for future programmable photonic devices: reversible optical properties (refractive index, \( n \), and extinction coefficient, \( k \)) by conducting cycles of light soaking and annealing. In the past, another family of amorphous materials e.g., As_{2}S_{3} chalcogenide glass has been used in photonics. By exploiting the photo-darkening effect in this material, the effective refractive index was varied by 1.3% around 1550 nm by visible light exposure: light-induced trimming of a coupled ring resonator filter was demonstrated.[8] However, in this case the trimming was permanent, which makes it only a direct write process without enabling erasing as a feature. Trimming and tuning by means of electro-optic and thermo-optic effects may avail the above-mentioned reversible programmable photonics, however, it is challenging due to the need for continuous compensating electronics, complicated processing, power consumption, and demand of high packing density of photonic devices.[9] This illustrates the value of materials that offer changing of optical properties in one direction and then reversing back to their original state, since these properties are desired for programmable photonic materials. Such a material...
can open up opportunities for new generations of photonic devices and photonic integrated circuits (PICs).

a-Si:H is known to have light-induced effects that are stable and reversible after annealing, which are therefore called metastable effects.\cite{10-14} Most notably, defects in a-Si:H can be created after prolonged exposure to light also known as light-induced degradation (LID), which can be recovered by annealing. This is commonly referred to as the Staebler–Wronski effect (SWE).\cite{14-16} Hereby it should be noted that the SWE is not equally pronounced in all types of a-Si:H and in some cases, e.g., the so-called polymorphous silicon (pm-Si:H), irreversible light-induced degradation has been reported.\cite{17,18} While metastable defect creation is considered a local effect on the scale of atoms and bonds, it has also been argued that this can manifest large scale structural changes.\cite{19} Furthermore, it has been reported that metastable volumetric expansion $\Delta V/V$ as high as $10^{-3}$ corresponds to large scale metastability.\cite{20-24} Therefore, it is natural to expect that these metastable structural effects should have metastable effects on the optical properties, which can be expressed in terms of $n$ and $k$. Hata et al.\cite{25-27} and Fortmann et al.\cite{28,29} indeed reported a slowly decreasing refractive index upon exposure with an above band gap light source. It was found that the light-induced effect was persistent after light soaking and reversible upon annealing below 220 °C for several hours. It was postulated that a reversible change in refractive index by 1–3% is possible. Recently, similar reversible light-induced behavior has been reported by Kim et al.\cite{30,31} Furthermore, Kuyken et al.\cite{32} showed that the non-linearity of a-Si:H nanowire waveguides was unstable during the characterization with a pump-probe technique at 1550 nm. Surprisingly, this phenomenon can be reversed after annealing at 200 °C for half an hour and this can be continued in cycles. However, no further systematic study into this reversible behavior has so far been published.

This work is aimed at studying the metastable optical properties of a-Si:H in a systematic fashion. We focus on the relation between material properties of a-Si:H films, such as atomic hydrogen content, microstructure, and nano-crystalline fraction, and the observed changes in optical properties due to high intensity light soaking and annealing. The imaginary part of the pseudo dielectric function $\varepsilon_2$, which can be obtained from a spectroscopic ellipsometry (SE) measurement, is sensitive enough to reveal light-induced changes and annealing effects after light soaking. This approach has an important benefit in terms of simplicity. A direct measurement of $\varepsilon_2$ can be conducted without employing any complex fitting model. Although the optical properties of the material cannot be obtained in full detail without using a fitting model, this simple approach that is employed here still enables a systematic study of the possible changes in the optical properties. Additionally, $\varepsilon_2$ is comparable to the imaginary part of the dielectric function $\varepsilon_2$ of a-Si:H around the peak position, since $\varepsilon_2$ directly represents $\varepsilon_2$ if the material is infinitely thick and perfectly smooth.\cite{33} This parameter is well established for analytical evaluation of the mass density.\cite{14,35}

Using this approach, we report here that high-intensity prolonged light exposure reduces $\varepsilon_2$ around electronic polarization resonance while $\varepsilon_2$ increases again after annealing for a set of a-Si:H thin films. This process can be performed in cycles. We also show that the light-induced changes in $\varepsilon_2$ and its reversal after annealing have a clear inverse relation with the atomic hydrogen content of the material. The magnitude of the reversibility of $\varepsilon_2$ is found to be as high as 3.7% at a photon energy of 3.6 eV for the densest film in this study, which implies that a-Si:H is an interesting candidate material for future programmable optical devices.

2. Experimental Section

a-Si:H films were deposited using an inductively coupled plasma enhanced chemical vapor deposition (ICP-PECVD) PlasmaLab 100 reactor from Oxford Instruments. Using silane (SiH₄) precursor gas diluted with argon (Ar), films were deposited at 600 W plasma power and 10 mTorr of reactor pressure. Several deposition temperatures (80, 150, 200, 250, and 300 °C) were used to achieve variations in hydrogen content and microstructure in the a-Si:H films. For a deposition temperature of 300 °C, the SiH₄ and Ar flow rates were both set to 30 sccm (50% Ar dilution). For the other deposition temperatures, the SiH₄ and Ar flow rates were set to 12 and 48 sccm, respectively (80% Ar dilution), such that the total gas flow is equal in all cases. Above 250 °C, 80% Ar diluted condition resulted in unstable films due to the high built-in stress. Generally, increased thickness or temperature-yielded unstable films which resulted in buckled delamination, a sign of extremely high compressive stress.\cite{36} Therefore, for the films deposited at 300 °C, the Ar dilution was reduced to 50%. All the films were between 240 and 250 nm thick and were deposited on undoped crystalline silicon wafers with (100) orientation.

The film thickness, pseudo dielectric functions, and optical properties were determined using a J.A. Woollam Co. M2000D rotating compensator spectroscopic ellipsometer (SE). The measurements were conducted between 1.24 and 6.5 eV at three different angles (65, 70, and 75°). All ellipsometric measurements (post-deposition, post-light soaking, and post-annealing) were performed ex situ in air at room temperature. The conversion of $\varepsilon_2$ from the SE-measured angles $\psi$ and $\Delta$ was done by the proprietary software CompleteEASE. For the sake of simplicity, we only report $\varepsilon_2$ for an incidence angle of 70°, because the $\varepsilon_2$ spectra for the other two incidence angles are comparable. Before deposition, each substrate was scratch marked to allow for measurements on the same spot after repeated light soaking and annealing treatments.

The atomic hydrogen content, microstructure parameter ($R'$), mass density, and refractive index in the infrared range of the spectrum ($n_{IR}$) were determined using a Bruker Tensor 27 Fourier Transform Infrared Spectroscopy (FTIR) setup in transmittance mode (between 340 to 7000 cm⁻¹). The crystallinity in the film was characterized using Raman spectroscopy measurements by a Renishaw Invia Raman Microscope equipped with a 514 nm laser (between 100 and 900 cm⁻¹) in backscattering geometry.

The light soaking treatment of the films was conducted with a home built setup with a concentrated LED 4000 K cool white lamp that produces a light intensity of 470 mW cm⁻². The sample holder was water cooled and maintained at 20 °C during light soaking. The annealing of the samples was done in a
vacuum oven in nitrogen (N$_2$) atmosphere at 180°C for 4 h. It was verified that for this annealing temperature the samples do not lose significant amounts of hydrogen during the annealing treatment and do not crystallize either.

3. Results

3.1. Film Characterization

FTIR spectroscopy is a popular technique that can be used to determine the atomic hydrogen content and the mass density of a-Si:H films.$^{37-43}$ This technique is also used to study the microstructure parameter which is indicative of the relative concentrations of vacancies and voids in the material.$^{37-40,42}$ The non-absorbing region (2200–7000 cm$^{-1}$) that contains interference fringes was used to determine the refractive index in the infrared part of the spectrum (n$_{IR}$) and the thickness of the film, as described elsewhere.$^{63}$ Silicon hydride (Si-H$_x$) characteristic vibration absorptions at wagging modes (630–640 cm$^{-1}$) and low and high stretching modes (LSM, $\approx$2000 cm$^{-1}$; HSM, $\approx$2100 cm$^{-1}$) are used to determine the atomic hydrogen content.$^{36-39}$ The wagging modes account for all the Si-bonded hydrogen in the film, while the LSM is associated with Si–H bonds in divacancies and the HSM is linked with Si–H bonds in larger vacancies and nano-sized voids. The density of a Si-H$_x$ mode $N_x$ is proportional to the integrated absorption strength ($N_x = A_x \int \omega^{-1} a(\omega) d\omega$, where $A_x$ is the proportionality constant of the given mode and $a(\omega)$ is the absorption coefficient). For the calculation of the atomic hydrogen content, we considered $A_{440} = 1.6 \times 10^{19}$ cm$^{-2}$ and $A_{LSM} = A_{HSM} = 9.1 \times 10^{18}$ cm$^{-2}$. The microstructure parameter $R'$ is defined as the ratio of the integrated absorption of the HSM to the sum of the integrated absorption of LSM and HSM together. This is a figure of merit indicating the fraction of Si–H bonds associated with large vacancies and nano-sized voids. Generally, microstructure parameter values below 0.1 are considered to indicate good material in terms of electrical properties and optical properties, as is relevant for instance in photonic devices.$^{4,44}$ Subsequently, the mass density of the material is determined using the Clausius–Mosotti equation, as described elsewhere.$^{37-41}$ These determined parameters for the temperature series of the different a-Si:H samples are shown in Table 1. As the deposition temperature increases from 80 to 300°C, the hydrogen content in the films decreases from 21.7 to 11.3%. Lowering of the atomic hydrogen content is typically observed when increasing the deposition temperature.$^{42,45}$ With the lowering of the

Table 1. a-Si:H thin film properties obtained from spectroscopic ellipsometry, FTIR, and Raman spectroscopy.

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>Deposition rate (Å s$^{-1}$)</th>
<th>Atomic hydrogen content (%)</th>
<th>Microstructure parameter ($R'$)</th>
<th>Mass density (g cm$^{-3}$)</th>
<th>Refractive index in the infrared, $n_{IR}$</th>
<th>Crystalline fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.5</td>
<td>21.7</td>
<td>0.13</td>
<td>2.11</td>
<td>3.26</td>
<td>10.0</td>
</tr>
<tr>
<td>150</td>
<td>1.3</td>
<td>18.9</td>
<td>0.12</td>
<td>2.13</td>
<td>3.31</td>
<td>8.2</td>
</tr>
<tr>
<td>200</td>
<td>1.3</td>
<td>17.1</td>
<td>0.10</td>
<td>2.15</td>
<td>3.33</td>
<td>7.4</td>
</tr>
<tr>
<td>250</td>
<td>1.2</td>
<td>15.9</td>
<td>0.07</td>
<td>2.16</td>
<td>3.35</td>
<td>3.7</td>
</tr>
<tr>
<td>300</td>
<td>2.7</td>
<td>11.3</td>
<td>0.06</td>
<td>2.18</td>
<td>3.38</td>
<td>4.1</td>
</tr>
</tbody>
</table>

When depositing a-Si:H films at high plasma power and moderate to high Ar dilution, it is known that this can induce crystallinity in the film.$^{36,46,47}$ Raman spectroscopy measurements employs a laser beam that can also induce crystallinity in a-Si:H when the laser intensity is too high.$^{48}$ Therefore, we have carefully chosen including moderate laser intensity to avoid crystallization during the Raman measurements simultaneously ensuring an acceptable signal-to-noise ratio. The Raman spectra for the temperature series are shown in Figure 1. The penetration depth of the green laser light (≈50 nm) is smaller than the thickness of the film, therefore the spectra only correspond to the a-Si:H films without seeing the influence of the substrate on the measurement. The crystalline fraction is determined by deconvolution of the Raman spectra between 400 and 560 cm$^{-1}$ with a peak fitting routine as reported elsewhere.$^{49-52}$ The longitudinal optical (LO) mode situated around 410 cm$^{-1}$ is approximated by a Gaussian distribution, as well as the transverse optical (TO) mode (470–490 cm$^{-1}$), and the boundary or intermediate phase components (490–510 cm$^{-1}$). The crystalline component is typically considered between 519
and 521.7 cm\(^{-1}\).\(^{[53]}\) The determined crystalline fraction is shown in Table 1.

As the deposition temperature increases from 80 to 250 °C without changing any other deposition parameters, the crystalline fraction decreases from 10 to 3.7% and this is clearly evident in Figure 1. For a deposition temperature of 300 °C, an increased SiH\(_4\) flow rate helps increase the deposition rate as shown in Table 1. However, the crystalline fraction is comparable to the film deposited at 250 °C. Note that ICP-PECVD has been reported to produce high-quality nano-crystalline silicon films at room temperature.\(^{[50]}\) Therefore, it is not surprising to find an increasing crystalline fraction with the decrease of deposition temperature.

The presence of crystallites is known to make hydrogenated nano-crystalline silicon (nc-Si:H) which is less susceptible to LID when compared to a-Si:H.\(^{[59]}\) However, in order to avoid a significant LID (and thus metastable electrical properties) in nc-Si:H, the crystalline fraction needs to be greater than 40%.\(^{[55]}\) Therefore, the set of a-Si:H films in this study can be considered more on the amorphous side while still including films with varying crystalline fractions. From our film characterization, it appears that the sample deposited at 300 °C is denser and contains the lowest amount of Si–H bonds residing at the inner surfaces of large vacancies and nano-sized voids. These attributes typically indicate a high electronic and optical quality of this a-Si:H material, which is also relatable to high photonic quality material.\(^{[4,44]}\) Furthermore, because of the lower crystalline fraction in the more amorphous films, the 300 °C material is more likely to show a significant metastability in the optical properties. Therefore, we first focus on this material for a detailed light soaking and annealing experiment, after which we discuss the results of the same treatment on the other samples.

### 3.2. Light Soaking Experiment

To study the high-intensity light-induced and annealing-induced changes in a-Si:H as a function of the a-Si:H atomic hydrogen content and microstructure, we inspect the imaginary part of the pseudo dielectric function \(<\varepsilon_2>\). The as-deposited film very slowly goes through surface oxidation after a long period of air exposure and as a result \(<\varepsilon_2>\) reduces and the peak shifts as shown in Figure 2(a).\(^{[25,56,57]}\) Therefore, for this study we considered twin samples deposited at the same time. One of them is considered as the reference which was stored at room temperature in ambient conditions to account for any surface oxidation-related changes without exposing this sample to light soaking or annealing treatments. SE measurement of this reference film was performed every time the corresponding twin sample was measured after light soaking or annealing.

LID is typically studied during 1000 h of AM1.5 light soaking at a light intensity of 1 sun (100 mW cm\(^{-2}\)) at 25 °C. In this study, we chose 450 h of light soaking at a light intensity of 4.7 sun as sufficient to get a near saturated change in the optical properties. After 450 h of light soaking, the sample deposited at 300 °C shows a clear difference from its reference counterpart. As shown in Figure 2(b), in addition to surface oxidation, \(<\varepsilon_2>\) decreases around the peak position with a small red shift, as has been reported elsewhere.\(^{[28,30,31]}\) After 4 h of annealing at 180 °C, the light-induced change is partially reversed with respect to its as-deposited state. However, compared to the reference, it shows a complete recovery to the reference values. From the FTIR measurement that was conducted immediately after deposition and also after repeated cycles of prolonged light soaking and annealing, no detectable change in the Si-bonded hydrogen content (either from stretching or wagging mode) was observed in the samples. Therefore, the annealing effect suggests a recovery of the light-induced effect that is not associated with a significant loss of hydrogen from the film. Although limited differences in the hydrogen effusion spectra before and after light soaking have been reported for pm-Si:H,\(^{[58]}\) this measurement technique is not widely known as a sensitive probe for light-induced changes in a-Si:H and since we did not detect any changes in the Si–H bonds based on FTIR spectroscopy, we have not resorted to hydrogen effusion measurements in this work. Different kinds of a-Si:H solar cells are known to exhibit room temperature annealing effect i.e., annihilation of light-induced electronic defects without resorting to high temperature annealing.\(^{[59,60]}\) However, we did not observe recovery of \(<\varepsilon_2>\) after light soaking or in between subsequent light soaking treatments that would suggest significant effects of room temperature annealing. For a period of 3 days we have observed the light-induced change in \(<\varepsilon_2>\) to be stable, making it metastable in nature.

The photon energy range shown with the peak of \(<\varepsilon_2>\) in the Figure 2 overlaps with the imaginary part of the dielectric function \(\varepsilon_2\) of a-Si:H. \(\varepsilon_2\) is related to both \(n\) and \(k\) (\(\varepsilon_2 = 2nk\)). Therefore, a reduced \(\varepsilon_2\) amplitude appears to suggest a reduced absorption due to reduced \(k\) (absorption coefficient, \(a = 4\pi k/\lambda\)) or a reduced \(n\) or a combination of both. These changes are reversed during annealing, such that the state of the reference film is approached again. An increase or decrease in absorption will reflect in a corresponding change in \(n\) according to the Kramers–Kronig relations, which describes the relation between \(n\) and \(k\). Because of this criterion, the real part of the pseudo dielectric function \(<\varepsilon_1>\) should also indicate light-induced
change and reversal after annealing. As expected, the $\varepsilon_1$ spectrum indeed shows a light-induced effect that is partially reversed after annealing as is clearly evident from Figure 3. However, the annealing treatment cannot completely reverse $\varepsilon_1$ back to the as-deposited state, at least to some extent due to the irreversible surface oxidation. The light-induced change in $\varepsilon_1$ and $\varepsilon_2$ and the reversal after annealing form an important observation, since it suggests that not only the extinction coefficient, but also the refractive index of $a$-Si:H can be reversible upon light soaking and annealing.

At photon energies below the range reported in Figure 2, fringes appear due to interferences from the interfaces due to the weak absorption of photons. These fringes are related to the refractive index in the far infrared range of the spectrum and the thickness of the film.[33] Figure 4 clearly shows the light-induced effect and reversal after annealing effects on the $\varepsilon_2$ spectrum for the lower energetic photon regime. It suggests that the reversibility of the optical properties is also viable in the low photon energy regime although small in magnitude compared to reversibility observed near the peak. The reason for this difference in magnitude is not clear, nor is it clear whether the thickness of the film plays a significant role here. However, this is a promising observation as it indicates that at the standard optical communication wavelength, around 1550 nm, we can also expect similar reversible optical properties by light soaking and annealing.

The reversibility of $\varepsilon_2$ can be demonstrated in cycles as is shown in Figure 5. After the first cycle of light soaking and annealing, the sample was exposed to further light soaking using the same conditions for 480 h. It is found that the light soaking and annealing have the same effect and dynamics when compared to the first cycle. Figure 5 shows the change in $\varepsilon_2$ at 3.6 eV for the reference and the light soaked/annealed sample over the course of the experiment with two cycles of light soaking and annealing. After the second annealing cycle it is clear that there is an absolute reversible difference ($\delta \varepsilon_2$) of 0.73 between the light soaked and annealed state measured at 3.6 eV, which is 0.72 after the first cycle. Within the experimental measurement error margin, this indicates a similar repeatable recovery of $\varepsilon_2$ for at least two cycles of light soaking and annealing. Relative to the annealed state, this reversibility corresponds to 3.7% at 3.6 eV. This is significantly higher than the previously reported 2% reversibility at 3.6 eV.[27] Note that, for confining and propagating light within a waveguide just 1% refractive index variation between the core and the cladding layer is already sufficient.[61] The error bars in Figure 5 were determined from the typical accuracy of the $\psi$ and $\Delta$ measurement by error propagation analysis using the closed expression for $\varepsilon_2$ as a function of $\psi$ and $\Delta$.[33] For the SE system used, the error of the $\psi$ measurement is 0.075°/C and the error of the $\Delta$ measurement is 0.05°/C. This error analysis makes it
possible to conclude that the relative changes in $\delta<e_2>$ are indeed significant and that $\delta<e_2>$ can be determined with an acceptable accuracy.

Similar to the sample deposited at 300 °C, the samples deposited between 80 and 250 °C, as shown in Table 1, were also systematically light soaked and annealed. After 480 h of light soaking, the samples were annealed using the same condition and duration as stated above. Also for these samples, no loss of Si-bonded hydrogen was observed after light soaking and annealing based on FTIR measurements. Similar to Figure 2–4, we have observed light-induced change and reversal after annealing for all these samples. However, the reversibility of the imaginary part of the pseudo dielectric function, which is quantified by $\delta<e_2>$, is found to be different for samples deposited at different conditions. As shown in Figure 6, there is a very clear inverse correlation between the film hydrogen content and $\delta<e_2>$. Apparently, as the film becomes denser because of a reduced void density (reduced $R^*$), the reversible light-induced change in $<e_2>$ increases.

3.3. Discussion

When comparing the light-induced changes in the imaginary part of the pseudo dielectric function spectrum with the reference (Figure 2), it could be inferred that there is an excess oxidation only in the case of the light soaked sample due to the high intensity of the light source. However, the fact that annealing reverses the light-induced change in $<e_2>$ and the fact that this change appears repeatedly in cycles of light soaking and annealing (Figure 5) suggests that the observed metastable pseudo dielectric function of a-Si:H is unlikely primarily due to surface oxidation. This is also confirmed by Figure 4, where the reversible $<e_2>$ upon light soaking and annealing is shown in the low photon energy regime. In this case, the penetration depth limitation of photons are unlikely to play a role. Therefore, the observed phenomena are most likely originating from the bulk. While we report the repeatable reversibility of the $<e_2>$ for two cycles of light soaking and annealing, it is currently unclear whether this repeated recovery can be preserved for a larger number of cycles as would be classically assumed for the SWE. If this is the case, it would pave the way towards photonic integrated devices that can be repeatedly written (programmed) and erased (reversed) for a large number of times. Although we do not have sufficient experimental data to indicate whether the recovery of $<e_2>$ is repeatable on the long-term, even a few cycles of repeatable reversibility of optical property can be sufficient to demonstrate the correct functioning of a programmable photonic device.

The metastability of a-Si:H is suppressed due to the presence of crystallites or non-hydrogenated regions in a-Si:H material.[12,54,55] It is therefore likely that the decreasing crystalline fraction for films deposited from 80 to 250 °C is the reason for the increasing reversibility of $<e_2>$ with decreasing crystalline fraction, as is depicted in Figure 6 and Table 1. However, for the samples deposited at 250 and 300 °C, the crystalline fraction becomes comparable, while the reversibility of $<e_2>$ is markedly different. This means that the crystalline fraction alone cannot explain the differences in $<e_2>$ changes as a function of the film growth temperature, since the variation in crystalline fraction is not very large. Consequently, one can assume that there is room for optimization and improvement of this metastable optical property of a-Si:H.

We have shown that the reversibility of the $<e_2>$ holds for the complete measured spectrum between 1.25 and 5 eV as shown in Figure 2 and 4. Still one observation needs addressing—the shift of the pseudo dielectric function spectrum due to light soaking. This red shift is in the same direction for both the light soaked and annealed sample as it is for the reference film. For the reference, this shift is attributed to the change in the surface morphology because of surface oxidation. Additionally, the refractive index is suggested to be reduced due to the oxide top layer which is why the $<e_2>$ near the peak reduces (Figure 2(a)).[56,62] The question is whether after light soaking, we are to expect a reduced $n$ and $k$, as $<e_2>$ near and beyond the peak also reduces for the light-soaked sample as depicted in Figure 2(b), meaning that the extra red shift is due to a morphological change. Agarwal et al.[63] reported changes in surface topology, i.e., increased roughness due to light-induced structural change, which has also been suggested by Fritzsch.[109] On the other hand, light soaking of a-Si:H is known to result in an increased amount of sub-bandgap defects according to the SWE.[64] As a consequence, increased sub-bandgap absorption is expected that increases $k$ with subsequent change in $n$. Therefore, answering this question is not straightforward and requires further experimental verification. We are currently in the process of investigating the metastable optical properties of a-Si:H around 1550 nm where standard applications of a-Si:H-based photonic are demonstrated.

4. Conclusion

We have demonstrated that the pseudo dielectric function $<e_2>$ of a-Si:H exhibits a metastable nature upon light soaking and
annealing, which suggests a reversible refractive index change that is likely originating from the bulk. Thus a-Si:H can be considered as an optically programmable photonic material. This is promising for optoelectronic and photonics integrated devices where a reversible refractive index modulation has potential for demonstrating future reversible programmable photonic devices. The magnitude of this metastable change in $\varepsilon_{2}$ is inversely correlated with the atomic hydrogen content of the materials. The reversibility of $\varepsilon_{2}$ is found to be as high as 3.7% (at a photon energy of 3.6 eV) for the densest film in this study, which is much higher than the previously reported 2%.27 Denser and largely amorphous material is favorable for programming, since it showed the largest reversibility. The findings from this work are of interest for the development of future programmable photonic devices, in particular when the reversibility of the optical properties can also be demonstrated in the near infrared range (around 1550 nm) which is the intended application spectrum for such devices.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

hydrogenated amorphous silicon, photonics, pseudo dielectric function, refractive index, spectroscopic ellipsometry

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