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Thermal stability of hot-wire deposited amorphous silicon

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Abstract

The material properties of hydrogenated amorphous silicon (a-Si:H) have been known to change when exposed to elevated temperatures. In this work we report on the thermal stability of the structural disorder, hydrogen content and defect structure of hot-wire deposited a-Si:H when exposed to temperatures in excess of 100 °C. Prior to thermal hydrogen diffusion a change in the defect structure is observed, caused by the creation of low concentrations of microvoids. There is evidence of vacancy clustering at 400 °C, caused by the alignment of unterminated Si dangling-bonds that consequently results in an increase in the defect size, concentration or both. Raman scattering shows evidence that no crystallization is induced at 400 °C and that the structural disorder increases upon annealing.
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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has proven to be of technological importance in applications such as solar cells, thin film transistors and liquid crystal displays [1–3]. However, in the manufacturing of the solar cells the intrinsic a-Si:H layer is usually subjected to further heat treatments, e.g. the post-deposition of the *n*- or *p*-doped layers. Furthermore, in subsequent use the solar cells may also be exposed to temperature cycling over a wide range of temperatures. Due to these complications, it is of fundamental importance to investigate the thermal stability of a-Si:H when exposed to elevated temperatures.

In this work we investigate the thermal stability of the hydrogen content and structural disorder, i.e. the critical factors that eventually determines the optical and electronic quality of a-Si:H [1], of hot-wire deposited a-Si:H when exposed to temperatures in excess of 100 °C. Additionally, the changes in the hydrogen content and structural disorder will be correlated with the changes in the defect structure, as investigated by Britton et al. [4,5].

2. Experimental details

The a-Si:H sample was deposited simultaneously on single-side polished <100> crystalline silicon (c-Si) and Corning 7059 substrates by the hot-wire CVD process, where SiH_4-gas is decomposed by the catalytic action of seven parallel tantalum wires at a temperature of 1600 °C. The substrate-to-filament distance and the separation distance between the wires amounted to 18 mm and 15 mm, respectively. The sample was deposited at a substrate temperature of 330 °C, which includes the contribution of both the substrate heater and tantalum wires, using 60 sccm SiH_4-gas under a deposition pressure of 2 Pa.

Isochronal annealing was performed under high-purity, flowing argon gas in a tube furnace at annealing temperatures ranging from 150−400 °C in 50 °C increments. The total annealing time amounted to 30 min for all temperatures. The ambient temperature at the sample position in the FTIR and Raman set-up amounted to 21 °C.

FTIR measurements were performed in transmission mode on the sample deposited on c-Si, using a DIGILAB FTS-40 FTIR spectrophotometer equipped with a liquid-nitrogen-cooled HgCdTe detector. The hydrogen content was calculated from the integrated absorption of the rocking modes of $\equiv Si-H$, $(=Si=H_2)_n$ and $-Si\equiv H_3$ using the

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procedures of Brodsky et al. [6] and proportionality constant proposed by Shanks et al. [7]. The error in the results is estimated to be within 15%.

Raman scattering measurements were performed in reflection mode on the sample deposited on Corning 7059, using the 514.5 nm line of a Spectra Physics Ar$^+$-ion laser. A detailed description of the Raman experimental set-up is described elsewhere [8]. The transverse-optical peak (TO) in the vibrational density of states of amorphous silicon reflects the degree of disorder in the amorphous network [9].

Doppler-broadening electron momentum spectroscopy was performed in situ at the above-mentioned annealing temperatures on the sample deposited on Corning 7059, using the continuous positron beam at the University of Cape Town [10], at an ambient temperature at the sample position of 68 °C. Positron lifetime spectroscopy was performed on the sample deposited on Corning 7059 in the as-deposited state and after annealing at 400 °C, using the pulsed positron beam at the Universität der Bundeswehr München [11]. A detailed description of the above-mentioned experimental procedures are described in detail elsewhere [4,5].

3. Results and discussion

Fig. 1 shows the temperature evolution of the infrared stretching band for the sample in the as-deposited state and after annealing at different temperatures. In the as-deposited state the stretching band is symmetrical around ~ 2000 cm^{-1}, indicating that hydrogen is bonded predominantly in the isolated phase as $\equiv$Si−H monohydrides [12]. No hydrogen migration from the isolated to clustered phase is observed as annealing progresses up to 400 °C, as seen from the continual symmetrical shape of the stretching band. This is indicative of H-atoms settling into more stable config-urations and consequently all the bonded hydrogen is expected to remain in the isolated phase.
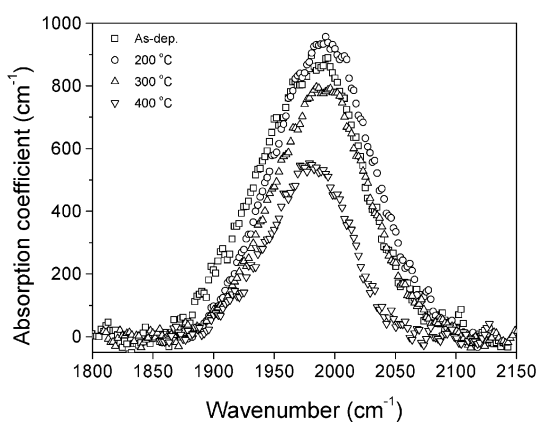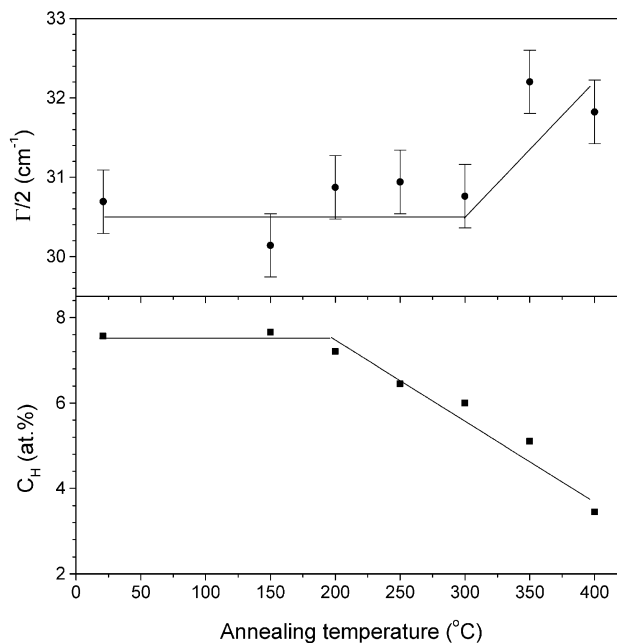
Fig. 2. Hydrogen content (■) and half-width-at-half-maximum of the a-Si TO-peak (●) as a function of annealing temperature.

Positron annihilation spectroscopy is a set of techniques based on the ability of positrons to become localized and eventually annihilated by nearby electrons when they meet open-volume imperfections (defects) in a solid [13]. Included in this set of technique is Doppler-broadening electron momentum spectroscopy that measures the momen-tum imparted to the annihilation quanta by the participating electron. Specific line-shape parameters can be used to quantify the fraction of positrons annihilating with different electron distributions. The low electron momentum fraction (S-parameter) depends primarily on the size and concen-tration of the defects and increases with an increase in the defect size, concentration or both [13]. Britton et al. [4,5] have investigated the development of the S-parameter on annealing at annealing temperatures ≤ 400 °C. The positron lifetime is dependent on the local electron density around

Fig. 1. Infrared stretching band in the as-deposited state (□) and after annealing at 200 °C (○), 300 °C (△) and 400 °C (▽).
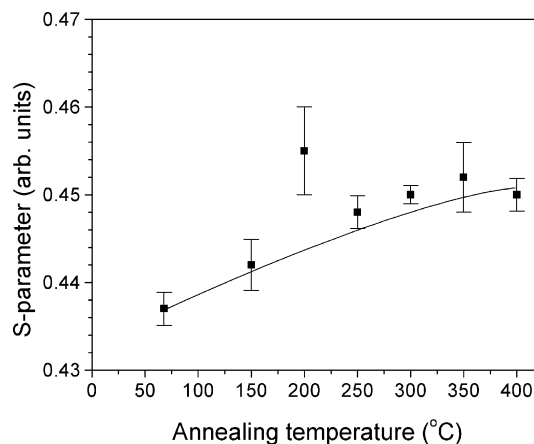
Fig. 3. Low electron momentum fraction (S-parameter) as a function of annealing temperature [4,5].
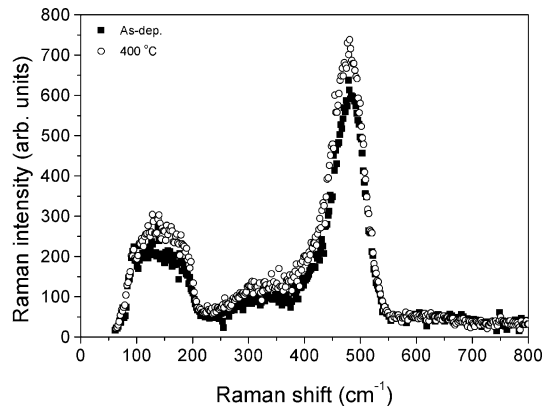
Fig. 4. Raman spectra in the as-deposited state (■) and after annealing at 400 °C (○).

the annihilation site. The defect-related lifetime, which is inversely proportional to the annihilation probability, increases as the electron density around the defect site decreases with increasing size. Therefore, positron lifetime spectroscopy is most sensitive to the defect size.

At temperatures ≤ 200 °C no considerable change in the hydrogen concentration C_H is observed (Fig. 2). In this temperature range an increase in the S-parameter is observed, as shown in Fig. 3 [4,5], indicative of an increase in the defect size, concentration or both. Since no hydrogen migration or diffusion is observed at temperatures ≤ 200 °C, the increase in the S-parameter in this temperature range can be attributed to the alignment of native Si dangling-bonds, which are already unstable at room temperature [13], and can therefore cluster to produce larger open-volume defects or microvoids.

At temperatures ≥ 250 °C a further increase in the S-parameter is observed (Fig. 3) [4,5], accompanied by a decrease in C_H (Fig. 2). The increase in the S-parameter is partly due to an increase in the number of defects, attributed to the creation of unterminated Si dangling-bonds. Furthermore, the native and/or unterminated Si dangling-bonds can again align to eventually cluster to form larger and/or more open-volume defects, thereby contributing to increased S-parameter. Positron lifetime spectroscopy confirms the absence of microvoids in the as-deposited state [4]. However, the formation of microvoids after annealing at 400 °C becomes evident, as seen by a second void-like lifetime component in the lifetime spectrum that amounts to 691 ± 54 ps [4].

The Raman spectra of the sample in the as-deposited state and after annealing at 400 °C are shown in Fig. 4. No emerging c-Si TO-peaks are observed at ~ 520 cm^{-1} before and after annealing, suggesting that no crystallization is induced as annealing progresses. An increase in the half-width-at-half-maximum of the a-Si TO-peak is observed after annealing at 400 °C (Fig. 2). This is indicative of an increase in the structural disorder [9], attributed to the

creation of the unterminated Si dangling-bonds and thereby resulting in an increase in the average bond angle variation.

4. Conclusion

FTIR and Doppler-broadening electron momentum spectroscopy confirm the creation of unterminated Si dangling-bonds with increasing annealing temperature. However, prior to hydrogen diffusion a change in the defect structure is observed and is caused by the creation of microvoids. Positron lifetime spectroscopy shows evidence of vacancy clustering at 400 °C, caused by the alignment of native and/or unterminated Si dangling-bonds that consequently results in the creation of more and/or larger open-volume defects. Raman scattering confirms that no crystalline phase transitions are induced at 400 °C and that the structural disorder increases on annealing.

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