ELSEVIER

Journal of Non-Crystalline Solids 227–230 (1998) 128–132

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Structural defects and hydrogen clustering in amorphous silicon

S. Acco [a,*], D.L. Williamson [b], S. Roorda [c], W.G.J.H.M. van Sark [a], A. Polman [d], W.F. van der Weg [a]

[a] Debye Institute, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, Netherlands
[b] Department of Physics, Colorado School of Mines, Golden, CO 80401, USA
[c] Group de Recherche en Physique et Technologie des Couches Minces, Département de Physique, Université de Montréal, Case Postale 6128 Succursale Centre-Ville, Montréal, QC H3C, Canada
[d] FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, Netherlands

Abstract

We have studied by small angle X-ray scattering the structural evolution on the atomic and nanoscale of hydrogenated amorphous silicon prepared both by ion implantation and by plasma-enhanced chemical vapor deposition and containing a similar H content. Results show that the initial structure of both samples is homogeneous on the nanoscale. Upon annealing, low-density features on the nanometer scale nucleate in both materials. However, the volume fractions of the nanoscale H-rich defects detected upon annealing and the temperature range of their evolution differ in the two cases. We propose that the initial structural disorder state of the matrix determines the initial H configurations and thereby their evolution upon annealing. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous silicon; Structural defects; Hydrogen clustering

1. Introduction

The effect of hydrogen on the short- and medium-range order of the amorphous silicon structure has been considered an important issue in amorphous silicon (a-Si) research [1,2]. Previous investigation [3] of hydrogenated a-Si made by ion implantation has shown that only a limited concentration of hydrogen atoms can be accommodated into the Si network and can evolve upon annealing from the Si bonds while remaining dissolved in the matrix. This H concentration defines the solubility for H in a-Si, which has been found to lie at ~4 at.%. When this H concentration is exceeded, the alloy structure is unstable and, upon annealing, nanoscale H-rich defects nucleate and grow in size [3]. The implications of a H solubility intrinsic to the a-Si network in deposited hydrogenated a-Si (a-Si:H) bear considerable importance, in light also of a better understanding of the twofold role of H in defect passivation and defect creation [4].

In order to gain insight into the process of H clustering and its dependence on the existing defect structure, we have compared the amorphized material (i.e., made by ion implantation), characterized by a highly disordered state, with device quality a-Si:H prepared by plasma-enhanced chemical vapor deposition (PECVD), which exhibits a low defect structure, but has a similar initial H content.

* Corresponding author. Fax: +31-30 254 3165; e-mail: s.acco@fys.ruu.nl

0022-3093/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII: S0022-3093(98)00219-1

2. Experimental

2.1. Sample preparation

An 8.5-μm-thick amorphous layer was prepared by multi-energy Si implantation of a 75-μm-thick crystal Si wafer. The amorphized layer was then irradiated with H_2 ions at 19 different energies ranging from 50 to 500 keV/amu. Hydrogen peak concentration was 12 ± 1 at.%, as measured by secondary ion mass spectrometry. All implants were carried out with the target held at liquid nitrogen temperature. Implanted samples will be referred to as the MH [or a-Si(H)] samples. MH indicates a *medium* H content that falls in between that of the LH (lower H) and HH (higher H) samples previously studied [3].

Device-quality intrinsic a-Si:H films were produced using plasma-enhanced chemical vapor deposition (PECVD). Films were deposited with a substrate temperature of 250°C by using a mixture of SiH_4 and H_2 at the ratio 1:1. A film deposited under identical conditions was used as the intrinsic layer to make a single-junction solar cell with a 10% initial efficiency [5]. High-purity aluminum foils were used as substrates. The H content was 11 at.%, as measured by elastic-recoil detection. It is important to note that the H concentration in this film is comparable to that of the peak values in the hydrogenated sample made by ion implantation. PECVD films will be referred to as the GD (or a-Si:H) samples.

Ion-implanted and deposited layers were subjected to subsequent anneals up to 4 h at temperatures ranging from 200° to 500°C, in 50°C increments up to 400°C and in 25°C increments for higher temperatures.

2.2. Small-angle X-ray scattering

Implanted and deposited samples were measured before and after annealing cycles by small-angle X-ray scattering (SAXS). The SAXS experiments were performed in a line-collimated set-up, described elsewhere [6], using monochromatized Cu K_α radiation ($\lambda = 0.154$ nm). The count rate was recorded as a function of the momentum transfer $q = (4\pi/\lambda)\sin\vartheta$ (2ϑ = scattering angle) from about 0.1 to 6 nm^{-1}.

The SAXS intensity $I(q)$ can be expressed as the sum of three different contributions [6]:

$$I(q) = I_D(q) + I_M(q) + I_P(q), \quad (1)$$

where $I_D(q)$ is the diffuse scattering, $I_M(q)$ the scattering intensity from electron density fluctuations on the nanoscale, and $I_P(q)$ represents the Porod term. This last term can account for a sharp rise of the signal in the smaller-angle region and it is indicative of density fluctuations on a much large scale (> 10 nm). In line-collimated geometry, $I_P(q) = A/q^3$, where A is the Porod constant.

The diffuse scattering intensity, $I_D(q)$, originates from atomic-scale density fluctuations: Compton scattering, thermal diffuse scattering, static disorder, and alloy scattering [7]. In the SAXS region, all these contributions are essentially angle-independent. We consider now the alloy scattering term. Hydrogen atoms introduce compositional fluctuations which yield the Laue monotonic scattering. Under the assumption of a binary random alloy, the Laue scattering (I_{Lm}) can be expressed in electron units (e/a) by [3]:

$$I_{Lm}(q) = x(1-x)(Z_H - Z_{Si})^2 \times \left[1 - \frac{1 - \Omega_H/\Omega_{Si}}{\gamma}\right]^2 (\text{in e/at.}) \quad (2)$$

where x is the H fraction, Z_H and Z_{Si} the atomic numbers of the relative elements, and γ is a constant including the Poisson's ratio. Ω_H/Ω_{Si} is the ratio of atomic volumes of the two elements [3,7]. From Eq. (2), it follows that the Laue scattering intensity is proportional to the H fraction in the alloy. Deviations from Eq. (2) are indicative of an alloy clustering, for instance, the presence of polyhydride or clustered monohydride groups.

3. Results

Fig. 1 shows the SAXS intensity (in e/a) as a function of the momentum transfer, q, for the H-implanted a-Si MH sample in the initial state and after subsequent annealing at various temperatures. The scattering intensity for the sample in the as-implanted state and after annealing up to and including 250°C (not shown) exhibits no q dependence. This

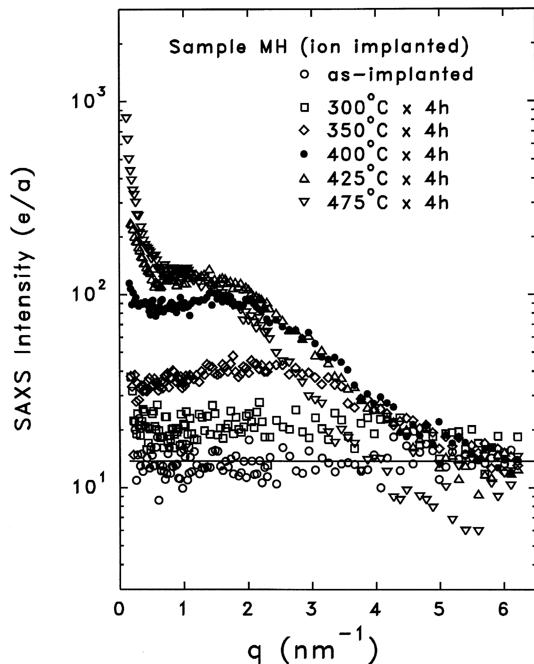

Fig. 1. SAXS intensities from the H-implanted a-Si MH sample in the as-implanted state and after subsequent annealing for 4 h at various temperatures. The line through the data of the as-implanted sample is drawn to guide the eye.

implies that, first, the signal contains only diffuse SAXS, which originates from atomic-scale density fluctuations. Second, nanoscale inhomogeneities, if present, are well below 0.1 vol.%. To examine the variation in the diffuse scattering intensity upon annealing, the data of each scan were averaged in the range $1.5 \leq q \leq 6$ nm^{-1}. Results are reported in Fig. 2. For comparison, the diffuse intensities originating from c-Si and as-implanted pure a-Si are also shown [7]. Annealing at 200°C does not cause any detectable change in the SAXS diffuse intensity of the MH sample, while an increase is evident after annealing at 250°C (Fig. 2).

As a result of annealing at 300°C, the scattering intensity increases and exhibits a weak q dependence (Fig. 1). This dependence corresponds to the formation of low-density structural features on the nanoscale, which have a q-dependent scattering function in the small angle region. The SAXS signal for the 300°C-annealed MH sample is consistent with the presence of ~ 0.15 vol.% of low-density nanoscale structural defects of 0.5 ± 0.05 nm average radius. Heating above 300°C produces a systematic increase in the SAXS signal, which demonstrates an increase of the volume content of the inhomogeneities (Fig. 1). After the annealing at 475°C, the volume fraction of the particles increased to ~ 0.6 vol.%. The steeper rate of fall-off of the intensity vs. q with higher anneal temperatures demonstrates growth of the particles. After annealing at 475°C, the average radius of the inhomogeneities increased to 0.94 ± 0.05 nm. For samples annealed at $T > 350$°C, it was necessary to add the Porod term in the fitting of the data to account for the observed increase of the intensity at smallest q (Fig. 1).

The increase of the SAXS signal upon annealing at $T > 300$°C occurs concurrently with the reduction of the diffuse scattering component, observable in the larger q portion of the data in Fig. 1. This reduction agrees with a H loss from the matrix or a reduction of the alloy clustering, which causes a decrease of the Laue monotonic scattering [8].

Fig. 3 presents the SAXS intensities from the a-Si:H GD sample in the as-deposited state and after various thermal treatments. As a general observation, all the signals exhibit a strong rise at smaller angles ($q \leq 1$ nm^{-1}), indicative of larger-scale objects and for all fittings the Porod term was added in Eq. (1). A lower q signal is usually observed on a-Si:H [6]

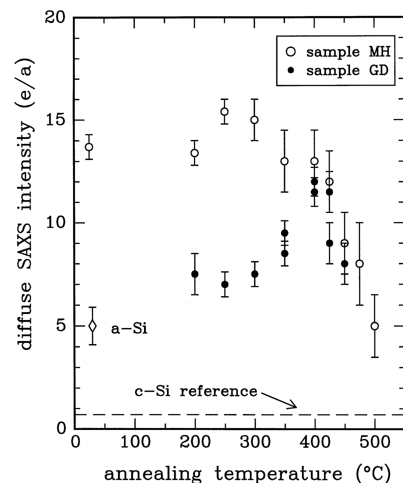

Fig. 2. SAXS diffuse intensity for the samples MH and GD in the initial state and after subsequent annealing at various temperatures. Annealing times were 4 h for the MH sample and from 1 to 4 h for the GD sample. We show also the value of the diffuse SAXS for c-Si and for the as-implanted pure a-Si from Ref. [7].

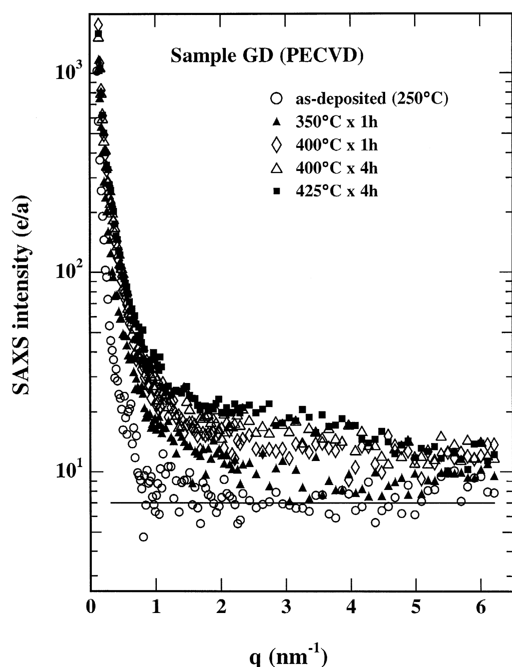

Fig. 3. SAXS intensities from the a-Si:H GD sample in the as-deposited state and after subsequent annealing at various temperatures. The line through the data of the as-deposited sample is drawn to guide the eye.

and its origin is discussed in more detail in a forthcoming paper [9]. Here, we consider on the portion of the data at $q > 1$ nm^{-1}. A very low scattering intensity with essentially no q dependence characterizes the signal of the deposited film in the initial state ($T_s = 250$°C). Annealing at temperatures up to the deposition temperature does not produce any change in the SAXS intensity. Results indicate once again that the signal consists of only diffuse scattering and therefore that low density nanoscale fluctuations are less than the detection limit in this temperature regime. Similar to the implanted sample, averages of the SAXS data in the 1.5–6 nm^{-1} q-range were calculated and are compared with those of the MH sample in Fig. 2.

Thermal treatments at temperatures higher than 300°C modify the structure of the film. The diffuse scattering increases after annealing up to and including 400°C, and is followed by a decrease at higher temperatures (Fig. 2). After annealing above 350°C, a q dependence is clearly visible in the SAXS signal (Fig. 3). Results therefore show that nanoscale inhomogeneities appear in the high-density bulk. Data associated with the sample annealed at 400°C for 4 h are consistent with ~ 0.10 vol.% of inhomogeneities of 1.2 ± 0.3 nm average radius. The volume content of these nanoscale particles increases following annealing at higher temperatures.

4. Discussion

Results indicate that nanoscale inhomogeneities, i.e., voids or H-rich clusters, if present, are less than the present SAXS detection limit of 0.01 vol.% in the as-prepared state of both the ion-implanted and the PECVD sample (Figs. 1 and 3). In addition to the homogeneity of the nanostructure, infrared absorption measurements [9] show that in both samples the H atoms are bound to Si primarily in monohydride configurations. We observe, however, differences on the atomic-scale disorder state in the two materials. The diffuse scattering is almost a factor of two larger in the MH sample than in the GD sample (Fig. 2). Based on the discussion in Section 2, we attribute this to differences in the static disorder and in the Laue scattering. The static disorder is expected to be larger in the MH sample than in the GD sample, in agreement with Raman scattering studies [9], which show a minimally and a maximally disordered network for the GD and the MH samples, respectively. In addition, the SAXS diffuse scattering (Fig. 2) suggest a higher degree of alloy clustering and/or a larger amount of atomic-scale vacancy-like defects in the implanted material compared with the a-Si:H film [9].

When comparing the evolution upon thermal treatments of the two materials, one of the most striking results is the qualitatively similar behavior of the structural modifications. Similar to the H-implanted material, two annealing regimes are distinguished in the a-Si:H. The first regime is characterized by changes of the atomic-scale structure, presumably related to an increase of alloy clustering. In the second regime, nanoscale inhomogeneities form and increase in content with annealing temperature. We note, however, that the temperature range for the two regimes is different in the two cases. Nanoscale low-density defects are visible after annealing at $T > 250$°C in the MH sample, while tem-

peratures higher than 350°C are needed in the GD sample. Furthermore, the volume fractions of the inhomogeneities of the GD sample remain much less than those of the MH sample at any temperature regime (Figs. 1 and 3).

The thermal instability of the structure of hydrogenated a-Si made by ion implantation and containing ~12 at.% H is not a surprising result and confirms our previous investigation [3] on a-Si(H) containing 20 and 4 at.%, respectively. Results indicated ~4 at.% as the H solubility in amorphized Si. Hydrogen-implanted a-Si with 4 at.% H was found to have a stable network structure that remained homogeneous upon annealing [3]. The presently investigated H-implanted sample contains H in excess of the solubility limit and it is therefore unstable against inhomogeneity formation. Nanoscale hydrogen complexes observed in implanted a-Si(H) were attributed to a process of H_2 formation followed by a coalescence into H_2-nanobubbles [3]. The similarity of the evolution of the H-implanted a-Si with that of a-Si:H leads us to assume that, also in the a-Si:H film, hydrogen precipitates upon annealing into nanoscale complexes. In other words, the appearance of inhomogeneities at $T \cong 400$°C in the PECVD material suggests that 11 at.% H exceeds the solubility limit in this temperature regime.

5. Conclusions

In this work, we have investigated the evolution upon annealing of a hydrogen-implanted amorphized silicon and device-quality PECVD a-Si:H film. Results show that, for deposited a-Si:H, annealing of an initially homogeneous structure on the nanometer scale leads to a process of H clustering, followed by a precipitation on a larger scale, similar to that of implanted a-Si(H) containing H in excess of the solubility limit. However, the degree of H clustering is much lower than that observed in the implanted samples. Ion-implanted a-Si(H) and a-Si:H have a maximally and a minimally disordered state, respectively. Therefore, despite the initial similar hydrogen concentration, the initial defect state and degree of disorder determine the initial H configurations in the network and thereby their evolution upon annealing.

Acknowledgements

We gratefully acknowledge W.C. Sinke for valuable discussions. This work was financially supported from the Netherlands Organization for Scientific Research (NWO). The work at the CSM was supported by the National Renewable Energy Laboratory under subcontract No. XAN-4-13318-04.

References

[1] N.H. Nickel, W.B. Jackson, Phys. Rev. B 51 (1995) 4872.
[2] Y. Hiroyama, T. Motooka, R. Suzuki, Y. Hirano, F. Sato, Appl. Phys. Lett. 68 (1996) 3126.
[3] S. Acco, D.L. Williamson, P.A. Stolk, F.W. Saris, M.J. van der Boogaard, W.C. Sinke, W.F. van der Weg, S. Roorda, P.C. Zalm, Phys. Rev. B 53 (1996) 4415.
[4] E.A. Davis, J. Non-Cryst. Solids 198–200 (1996) 1.
[5] W.G.J.H.M. van Sark, J. Bezemer, R. van der Heijden, W.F. van der Weg, Mater. Res. Soc. Symp. Proc. 420 (1996) 21.
[6] D.L. Williamson, Mater. Res. Soc. Symp. Proc. 377 (1995) 251.
[7] D.L. Williamson, S. Roorda, M. Chicoine, R. Tabti, P.A. Stolk, S. Acco, F.W. Saris, Appl. Phys. Lett. 67 (1995) 226.
[8] L.H. Schwartz, J.B. Cohen, Diffraction from Materials, Springer, Berlin, 1987, p. 402.
[9] S. Acco, D.L. Williamson et al., submitted.