Journal of Non-Crystalline Solids xxx (2011) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Order and disorder in edge-supported pure amorphous Si and pure amorphous Si on Si(001)

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ARTICLE INFO

Article history:
Received 17 September 2010
Received in revised form 1 February 2011
Accepted 1 February 2011
Available online xxxx

Keywords:
Ion-implantation amorphization;
Amorphous silicon;
Low angle X-ray scattering

ABSTRACT

We report results from an investigation into hidden anisotropy in pure fully-dense amorphous silicon. For amorphous silicon in intimate contact with a crystalline Si(001) substrate, one can reasonably expect that the interface with the substrate may impose anisotropy in the form of distorted ordering within the film. Indeed, we found four-fold periodic intensity variations, with bimodal intensity centered along the substrate c-Si <110> directions, in the X-ray scattering from a-Si on Si(001). These well-defined intensity variations disappeared entirely in X-ray scattering from edge-supported a-Si films, where there was no detectable anisotropy.

1. Introduction

The current research was undertaken as part of a search for hyperuniform ordering [1] in amorphous silicon. Hyperuniformity imposes an additional criterion on disordered structures, raising the bar on the need to assure that the measurements are performed on high quality isotropic samples. Pure amorphous silicon is a highly strained material, and it is far from obvious that the atomic scale structure of freestanding edge-supported samples will consist of isotropic non-crystalline continuous random network packing. Amorphous silicon is usually prepared by means of vapor deposition or crystal disordering. Of these two methods, disordering a silicon crystal by means of self-ion implantation has proven capable of creating appreciably thick (of order 10 μm) amorphous films with high purity and low porosity [2]. Such films can subsequently be relieved of the substrate by selective chemical etch of a portion of the underlying substrate. While it is well known that a crystal can impose ordering on an attached film, it is not clear whether any imprint of the single crystal remains after the amorphous film is freed from the substrate. We report here sensitive X-ray scattering measurements to determine whether there is any memory in the disordered structure of the edge-supported amorphous film that recalls the single crystal substrate from which it was produced.

Previous investigations of amorphous-Si, prepared by means of vapor deposition onto single crystal silicon, were carried out by means of transmission electron microscopy, where the authors suggest the existence of nanocrystalline ordering at the interface with the crystalline substrate [3]. While the interpretation of the data was questioned subsequently [4], the possibility was not explicitly ruled out. Castro-Colin et al. [5,6] investigated thermally grown SiO_2 on Si(001), and found that the vitreous film was deformed along substrate <110> directions, where it became significantly more dense along those directions than in the bulk of the film. They were further able to show that the observed fourfold intensity modulations decayed away from the film-to-crystal interface. They modeled their observations with a compressed interfacial region consisting of highly distorted pseudo-coesite growing in registry with the Si <110> and Si $<\bar{1}\,\bar{1}\,0>$ through the film. The variations in density are regarded as clear evidence of the loss of isotropy of amorphous SiO_2 when in contact with a highly symmetric Si(001) substrate.

The current research is aimed at gaining an understanding of the likely orienting effect on an amorphous silicon film at its interface with a single crystal silicon substrate. If ordering occurs, to what extent does it remain in the amorphous film after it is freed from the substrate? Whereas Castro-Colin et al. [5,6] made use of grazing incidence scattering and sample rotation about the perpendicular to <001> to probe their thin (100 Å and 500 Å) SiO_2 films, we made use of X-ray scattering in transmission. This made it possible for us to measure directly the two-dimensional (2D) azimuthal distribution of scattering intensity of our thicker (of order 10 μm) samples over nearly a full 360°.

2. Experimental

Our samples are two well-characterized [7,8] nearly-fully-dense (99.9% TD +) pure a-Si samples prepared by means of self-ion

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doi:10.1016/j.jnoncrysol.2011.02.003

implantation at 13 different energies and fluences [2] into a single crystal Si(001) wafer at 77 K. One sample was as-implanted and the other was annealed in vacuum at 600 °C for 1 h to induce structural relaxation. A wet chemical etch was applied to a 5-mm-diameter area in the center of the back of each 2 cm × 2 cm wafer, removing the c-Si and leaving an edge-supported freestanding membrane of pure a-Si. This procedure produced two unique samples, each consisting of an edge-supported 5-mm-diameter a-Si membrane in the center and a substrate-supported a-Si membrane on a large portion of the rest of the wafer. Earlier diffraction measurements [7,8] on the same samples provided $S(q)$ over an extended scattering vector, q, range out to 55 Å^{-1}. Both the as-implanted sample and the annealed (relaxed) sample have similar first-shell coordination number close to 4. In the earlier X-ray scattering measurements, as well as the present experiment, the primary scattering peak from the annealed (relaxed) sample was more intense and narrower than that from the as-implanted sample, demonstrating that the films have been remarkably stable over time.

SAXS/WAXS measurements of the two a-Si samples were performed at the Advanced Photon Source (APS) 5ID-D experimental station. 17 keV X rays were used, with a sample-to-detector distance of 280 mm or 293 mm. This arrangement enabled us to cover a q range from approximately 0.1 to 2.5 Å^{-1}. The brilliant source of X rays made it possible to obtain excellent counting statistics on the primary diffraction peak from a-Si at $q = 1.98$ Å^{-1}, so that we could perform a sensitive search for loss of isotropy within the amorphous film by monitoring intensity fluctuations around the primary diffraction peak ring. In addition, if nano-nucleation were present, it would be detected through the appearance of tiny very sharp (111) diffraction features on the broad primary diffraction peak. In this manner we were able to ensure that the measured scattering volume is free from nucleation of nanocrystalline Si. To be clear, we will not consider ordering at the 1 nm level to be nanocrystalline.

The samples were mounted in a vacuum chamber in front of a MAR-165 image plate detector. In this way the measurements avoided parasitic scattering from air and window materials. Corrections were made to the data for detector dark field, empty beam, absorption and X-ray polarization. We performed an absolute intensity calibration by means of a glassy carbon secondary standard previously calibrated on the primary calibrated APS Ultra Small Angle X-ray scattering (USAXS) instrument [9]. In addition, we used scattering from a rotating glassy carbon sample to verify the polarization correction and to characterize the MAR-165 image plate detector. Making use of earlier published data [7,8] on these samples, our final intensity adjustment was made using the thickness of the samples. Absolute calibrated USAXS data indicated sample thicknesses from 9 to 13 μm for different positions of the X-ray beam on the a-Si membranes, where this last free parameter was within the limits set by our earlier measurements. For the a-Si on wafer samples, the data reduction procedure was the same but the intensities were not corrected for the absorption by the wafer.

3. Results

Scattering from edge-supported annealed (relaxed) a-Si and annealed (relaxed) a-Si on Si(001), and original 2D images of the X-ray scattering from each are shown in Fig. 1. The primary diffraction peak centered at $q = 1.98$ Å^{-1} appears in the 2D data as a broad white ring near the edge of the detector. The 2D scattering from the edge-supported a-Si is easily seen, while scattering from the a-Si on Si(001), still clearly observable, is less intense as this data is not corrected for X-ray absorption by the wafer. For the a-Si on Si(001), Kikuchi lines are visible in the central part of the image.

The corrected 2D data offers straightforward access to an analysis of structural isotropy, or the lack thereof, by examining the scattering intensity around the maximum of the primary diffraction peak as a function of azimuthal angle. Although there is no obvious variation in the annular distribution of scattered intensity in either of the 2D images in Fig. 1, upon closer examination we find that there is considerable systematic variation as seen in Fig. 2. There is a complicated pattern of scattering from both samples, where we have indicated with arrows the positions of the Si <110> directions in the substrate. Although the data in Fig. 2 are from samples with the same orientation, we also performed scattering measurements where the orientation of the annealed (relaxed) sample was rotated by 45° with respect to the orientation of the as-implanted sample; the intensity pattern rotated accordingly. The measurements were repeated at another X-ray energy (16 keV), and repeated again with the incident X-ray beam on the film, instead of on the substrate, and finally with an as-implanted sample of different film thickness (2.06 μm). Intensity variations at q-values on the shoulders of the peak showed the identical pattern to that measured at the maximum. Indeed, the scattering results were always the same. The only change

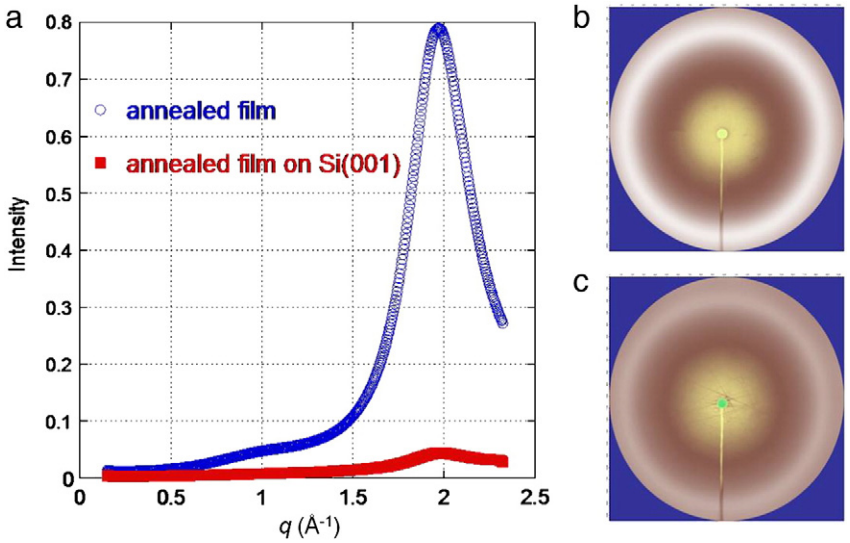

Fig. 1. (a) Scattering from edge-supported annealed (relaxed) a-Si (absolute scaled) and from annealed (relaxed) a-Si on c-Si(001) (uncorrected for absorption). (b) The 2D scattering from annealed edge-supported a-Si. (c) The 2D scattering from annealed a-Si on Si (001). In (b) and (c), the primary diffraction peak in the 2D data appears as a broad white ring near the edge of the detector. With the exception of the narrow post that supports the beam stop, there are no obvious intensity changes around the diffraction ring measured from either sample. The film thickness is 12.7 μm.

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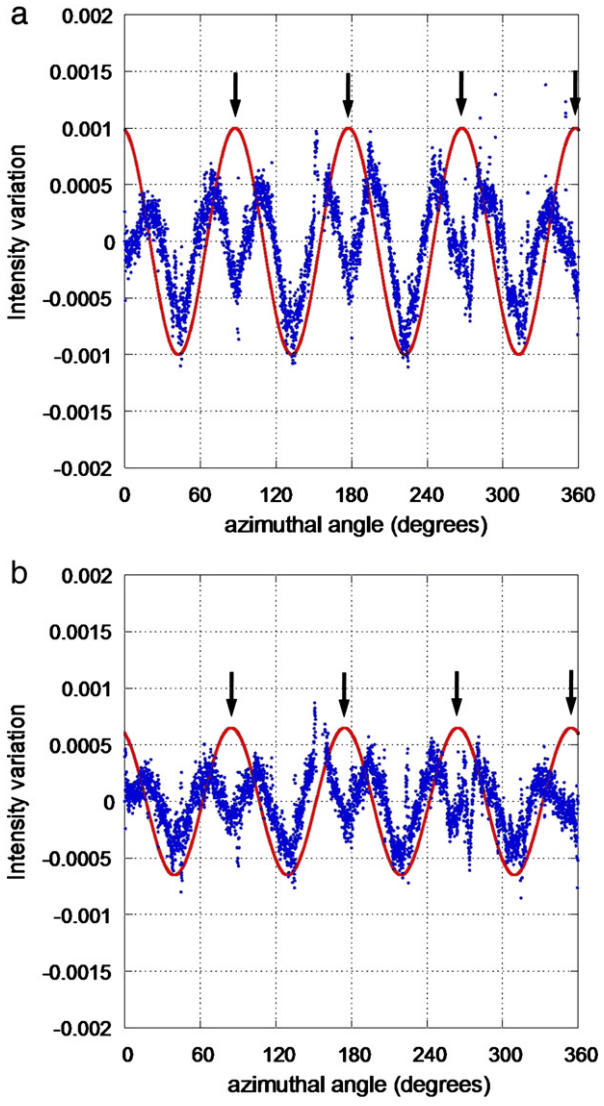

Fig. 2. Scattering intensity as a function of azimuthal angle of the primary diffraction peak maximum of (a) as-implanted a-Si on Si(001) and (b) annealed a-Si on Si(001). A complicated four-fold pattern is visible, with the center of each double-peaked feature along one of the <110> directions indicated with arrows. The solid lines emphasize the underlying four-fold nature of the peaks, even though the peaking is bimodal. The intensity variation is less for the annealed (relaxed) a-Si film on Si(001), but the proportion of 4-fold to 8-fold in the pattern is the same.

we saw was that the amplitude of the intensity variation is greater for the as-implanted a-Si on Si(001) than for the annealed (relaxed) a-Si on Si(001).

Although the intensity is centered along the <110> directions, there is a surprising dip in the center of each of the "peaks" in the four-fold pattern. Mathematically, this can be represented with a 4-fold plus an 8-fold pattern; calculating the combined intensity of a 4-fold plus an 8-fold sine wave, with the latter approximately 71% of the former in strength, we can model the intensity distribution. The result is shown in Fig. 3.

For the edge-supported a-Si films, there is no discernable azimuthal intensity pattern in the scattering from either the as-implanted or the annealed (relaxed). (Fig. 4)

4. Discussion and conclusions

The X-ray scattering results uncover the existence of a surprising pattern of anisotropy in a-Si on Si(001). Increased scattering intensity is centered on the four <110> directions along the crystal surface, with

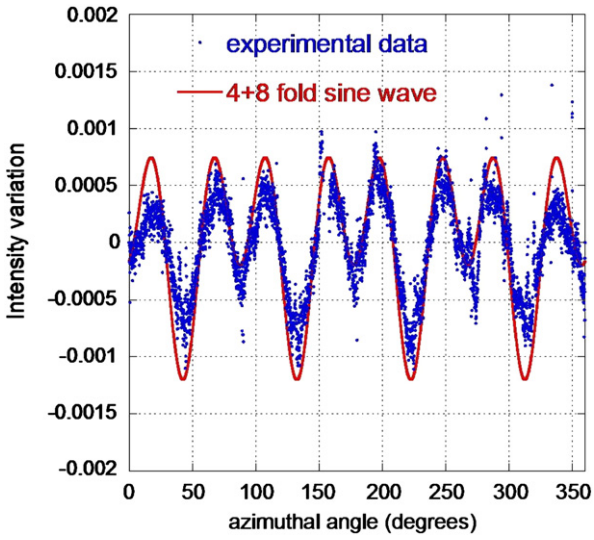

Fig. 3. Data and simulated primary peak intensity variation as a function of azimuthal angle for annealed (relaxed) a-Si on Si(001).

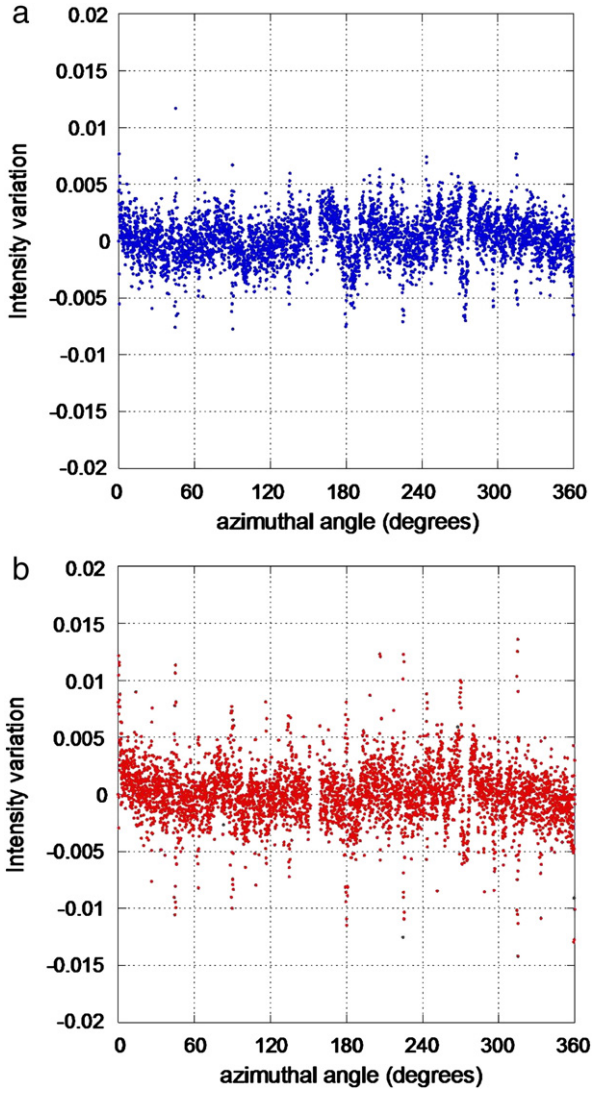

Fig. 4. Scattering intensity of (a) the primary diffraction peak maximum of the edge-supported as-implanted a-Si and (b) the annealed (relaxed) a-Si as a function of azimuthal angle. There is no visible remnant of the four-fold (plus 8 fold) pattern of the films on the substrate, demonstrating that the films are entirely isotropic.

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an unanticipated dip in the center of each peak. These results are very robust.

- A freshly prepared 12.4-μm-thick as-implanted a-Si sample scattered X rays in exactly the same pattern as the 11-year-old 12.7-μm-thick samples. Even where we observed that the intensity variation is somewhat less for the annealed (relaxed) sample than for the as-implanted samples, the proportion of 4-fold to 8-fold intensity is exactly the same.
- The amount of intensity variation is the same, independent of the thickness of the as-implanted film (2.06 μm or 12.7 μm), leading us to conclude that only the layers near the amorphous film-to-crystal substrate are affected.
- The observations are independent of sample orientation with respect to the incident X-ray beam, and with respect to the incident X-ray energy, indicating that dynamical diffraction effects in the substrate cannot be responsible for the dip in the center of the peaking along the <110> directions.
- The intensity variation is the same whether measured at the peak or at q-values on the wings of the primary diffraction peak, away from incipient Si(111), indicating the absence of nanonucleation on a scale too small to observe even tiny peaks.
- After the substrate is removed, there is no evidence of residual angular correlations or anisotropy of any kind in the freestanding edge-supported films.

The peaked scattering of a-Si on the Si wafer, even though it is bimodal, shows that the film is compressed along the <110> directions on the wafer surface. There is a softening of phonon modes along these directions, as noted earlier along with the observation of a similar but unimodal compression pattern in thin SiO_2 films grown on Si(001) [5,6]. In the SiO_2 case, the measurements were performed in reflection, and the intensity correlations were clearly visible in the raw data. Although the amorphous SiO_2 films were only 100 Å and 500 Å thick, Castro-Colin et al. [5,6] were able to show that the correlations decreased away from the interface. Also, as indicated above, the vitreous SiO_2 results differ from the a-Si results presented here in that there were no dips in the center of the scattered intensity peaks from the silica. The unimodal peaking in the vitreous SiO_2 intensity distribution was explained by the possible formation of deformed pseudo-coesite. In the case of a-Si, it may be that deformed nanoscale c-Si simply cannot form and therefore there are no candidate structures to fill in the intensity dips along the four c-Si <110> directions.

Pending the completion of detailed modeling of the anisotropy of a-Si, we propose that the increased intensity along <110> directions as well as the dips arise from force balance in the transition layer at the interface between a-Si and c-Si. On the slightly less dense a-Si side of the transition layer, the first layer of atoms is forced further from the interface and closer to each other. On the c-Si side of the transition layer, force balance requires the atoms to come closer to the interface and further from each other. We suggest that these effects together bring about the increase in scattering intensity and the dip in the center of the intensity peaks. In the edge-supported freestanding films, the effect of the crystal template disappears completely, and the films indeed distribute themselves uniformly.

Acknowledgements

Thanks go to Jan Ilavsky for his help with quick-look data analysis and the USAXS measurements at APS 32-ID-B, and to Rozaliya Barabash and Joseph Woicik for helpful discussions. SCM acknowledges support from the State of Texas through the Texas Center for Superconductivity at the University of Houston. This work was performed at DND CAT 5-ID-D at the Advanced Photon Source, Argonne National Laboratory. The APS is supported by the US DOE under contract #DE-AC02-006CH11357.

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