Increasing medium-range order in amorphous silicon with low-energy ion bombardment

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We have observed the existence of medium–range order in amorphous silicon with the fluctuation electron microscopy technique. We hypothesize that this structure is produced during the highly nonequilibrium deposition process, during which nuclei are formed and subsequently buried. We test this hypothesis by altering the deposition kinetics during magnetron sputter deposition by bombarding the growth surface with a variable flux of low-energy (20 eV) Ar^+ ions. We observe that medium–range order increases monotonically as the ion/neutral flux ratio increases. We suggest that this low-energy bombardment increases adspecie surface mobility or modifies local structural rearrangements, resulting in enhanced medium–range order via increases in the size, volume fraction, and/or internal order of the nuclei. © *2003 American Institute of Physics.*
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Amorphous silicon (a-Si) is an important semiconductor for large area applications such as thin film transistors and photovoltaics. A technique, fluctuation electron microscopy (FEM),[1] has revealed that a-Si is not a completely disordered covalent random network, as was historically thought. With the FEM technique, a-Si was found to contain significant medium-range order (MRO) on the length scale of 1–2 nm. MRO at such a scale is virtually impossible to detect with standard diffraction measurements, as these are only sensitive to two-body correlation functions. However, MRO is clearly visible in FEM, which is sensitive to the three- and four-body correlation functions.[1]

In FEM the statistical variance, V, of dark-field hollow-cone transmission electron microscopy (TEM) images taken at a MRO-scale (1.5 nm) microscope resolution is measured as a function of the diffraction vector magnitude k. All simulations performed to date[2,3] indicate that $V(k)$ and MRO are monotonically related and that a fine-grained, highly strained structure termed "paracrystalline" provides the best match to FEM data, whereas continuous random networks fail to do so.[4]

We hypothesize that the paracrystalline structure is produced during growth of a-Si via a frustrated polycrystalline growth surface: at low substrate temperatures (T_{sub}), crystalline nuclei are produced on the growth surface but are quickly buried by subsequent nucleation events. In the bulk these crystallites are forced into a strained, metastable state as the surface energy of the crystallites is different in the bulk than on the film surface. This strain, produced by grain boundary bonding constraints, shifts the atoms slightly out of crystalline register, but order at the medium-range remains. Larger or more ordered paracrystallites should therefore demonstrate greater MRO. When larger nuclei were produced via increased substrate temperatures during growth of a-Si, the MRO strongly increased.[5]

Initial simulations performed to probe the effect of paracrystallite sizes on FEM also demonstrated changes in the vibrational and electronic densities of states.[2,3] Therefore, in addition to FEM, we probe the the vibrational and electronic densities of states via Raman scattering and spectroscopic ellipsometry (SE).

In this work, we investigated the role that surface growth mechanisms play in producing MRO by keeping T_{sub} strictly constant (230 °C) and bombarding the growing film with a controllable flux of 20 eV Ar^+ ions. As these large, low-energy ions cannot penetrate more than 1–2 layers into the growing a-Si film, any observed changes in MRO can be assigned to a near-surface mechanism. In related work, we have used this ion bombardment technique at higher T_{sub} ($\sim$400 °C) to directly deposit polycrystalline Si with increased grain sizes, no a-Si incubation layer, and a very low surface roughness.[6] Ion-enhanced epitaxy experiments[7] show that low ion energy (20 eV) ion bombardment can dramatically improve epitaxy in otherwise prohibited temperature and thickness regimes. Recent simulations predict that recoils at energies as low as 3–15 eV can lead to significant athermal recrystallization.[8] Although the exact microscopic mechanism driving these effects is not understood, these effects are consistent with the hypothesis that low energy ion bombardment enhances adatom mobility or local structural rearrangements. These phenomena should lead to an increase in the MRO of the films if our hypothesis about MRO formation during growth is correct.

We have deposited thin a-Si films at 230 °C by dc magnetron sputtering of a Si target in a pure Ar plasma. This deposition technique is unique in that no hydrogen is present, unlike other a-Si deposition processes. Although hydrogen is

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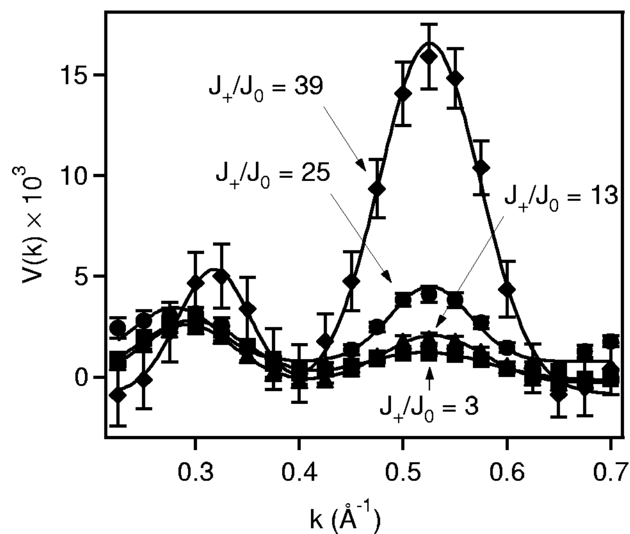

FIG. 1. Fluctuation microscopy variance data of 20-nm-thick a-Si at varying J_+/J_0.

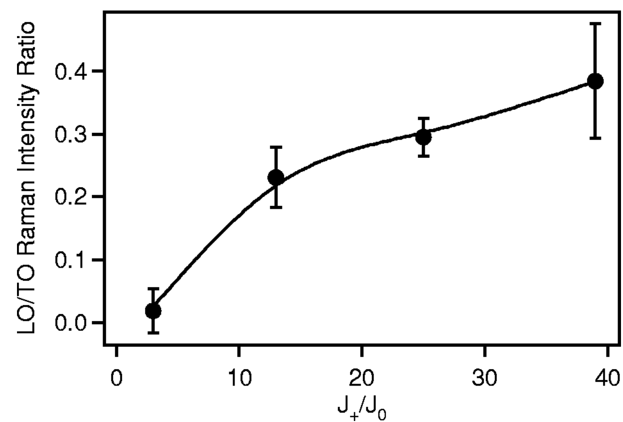

FIG. 2. Ratio of the LO to TO Raman modes of 200-nm-thick a-Si at varying J_+/J_0.

necessary to produce device quality a-Si, we purposely do not include it in this work as it complicates the structural analysis, and the paracrystalline model simulations do not yet consider it. Details of the deposition process are described elsewhere.[9] The sputter pressure was 1.8 mTorr at all times in order to preserve the energy of Ar^+ ions ($\sim$20 eV) and sputtered Si neutrals (median energy 10 eV) by reducing gas-phase collisions. An axial magnetic field was applied to the chamber via external Helmholtz coils, effectively unbalancing the magnetron. This collimates the plasma outside of the target region and increases the Ar^+ ion flux to the growing film. Ion to neutral flux ratios, J_+/J_0, of 3–39 are produced; J_+ and the plasma potential (V_p) were measured with cylindrical Langmuir probe techniques. During initial growth, the ion energy is equal to V_p due to the insulating substrate, and so the ion energy equals $V_p - V_{\mathrm{float}}$. Once a continuous film is deposited, the film contacts the substrate holder, which is biased at 20 V in order to limit the subsequent ion energy to approximately 20 eV. We chose this low energy as even slightly higher ion energies of $\sim$40 eV can introduce damage.[7,10] Temperature calibration measurements performed with a thermocouple attached to the surface of both glass and silicon substrates with ceramic paste verified that the bulk film temperature did not increase more than 1 °C during growth. It should be emphasized that the only parameter varied in the films presented here is J_+/J_0.

Thin (20 nm) films were grown on TEM-grade rock salt and floated off in de-ionized water onto Cu grids for FEM, and both thin (20 nm) and thicker (200 nm) films were grown on Corning 7059 glass for Raman scattering and SE analysis. Raman scattering was performed with the 514.5 nm line of an Ar^+ laser at 30 mW. SE was performed between 2.5 and 5 eV with a HS-190 J.A. Woollam Co., Inc. ellipsometer, and modelling was performed with the Woollam WVASE software.

Fluctuation microscopy data are presented in Fig. 1. The solid lines are gaussian fits to the data to guide the eye. The data show the characteristic pattern of amorphous silicon with MRO, with peaks at $k = 0.30$ Å^{-1} and $k = 0.55$ Å^{-1}. The variance of the TEM images increases monotonically with ion flux, indicating that there is more MRO in the films as the ion bombardment is increased. These data are similar, but with reduced magnitude, to those from a substrate temperature series of films, including the shift to higher k of the $k = 0.30$ Å^{-1} peak of the $J_+/J_0 = 39$ data.[5] We cannot yet determine if this increasing MRO is due to the increasing density, size, or order of paracrystallites; future work with the recently developed variable resolution mode FEM will explicitly probe the length scale of MRO.

Raman spectra were taken of both the 20- and 200-nm-thick films; the data from the 200 nm films only are discussed here due to a much improved signal to noise ratio. While all films appear amorphous in the Raman spectra, the film with the most MRO as determined by FEM has higher peaks in the longitudinal region only ($\sim$290,$\sim$380 cm^{-1}). This effect has been predicted by simulations of the vibrational densities of state as a function of paracrystallite size and density in computer models.[2] We observe no evidence of height or width variations in the TO peak, indicating that the short range order is not changing. In general, the TA/TO ratio, often used to estimate short range order, varies because the width of the TO band varies with bond angle distribution, simultaneously changing the TO peak height; the TA peak remains constant.[11]

To quantify the changes in the LO region, the spectra above $\sim$300 cm^{-1} were rigorously fit to three gaussians; this cutoff was used in order to completely remove the TA peak which was nongaussian and complicated the fitting. The results are presented in Fig. 2. The intensity of the LO/TO peak ratio correlates with MRO as determined by FEM, and therefore may provide another tool for evaluating MRO, if the signal to noise ratio is improved. To summarize, it appears that the TO band is sensitive only to short-range order, while the longitudinal bands are sensitive to medium-range order.

Spectroscopic ellipsometry data were taken, and the imaginary part of the pseudodielectric function ($\langle \varepsilon_2 \rangle$) extracted, which is shown in Fig. 3. Note, again, a monotonic effect: as FEM variance and the LO Raman modes increase, the $\langle \varepsilon_2 \rangle$ peak shifts down and slightly to the left. Simulations predict that there should be a change in the electronic density of states with changing MRO, as the valence band states localize on the paracrystallite grain boundaries.[3] However, similar changes in $\langle \varepsilon_2 \rangle$ can be caused by differences in void content, oxide thickness, or surface roughness of the

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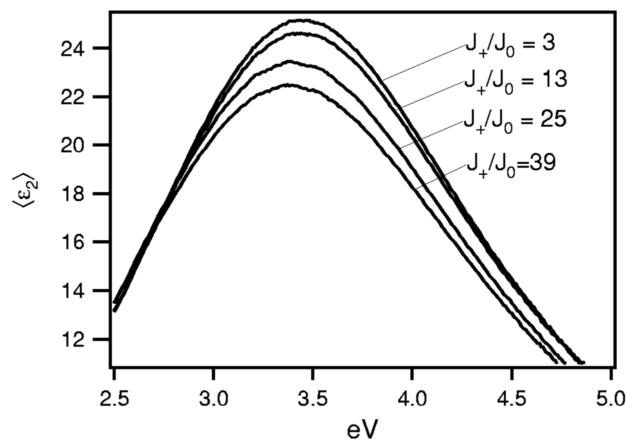

FIG. 3. Spectroscopic ellipsometry data of a-Si at varying J_+/J_0.

films. In order to clearly separate these very different effects in the SE spectra, we fit the data inclusively. Using the $J_+/J_0=3$ data as reference data, the $J_+/J_0=39$ data were fit to all possible combinations of the $J_+/J_0=3$ reference data, void content, surface roughness, and surface oxide layer thicknesses. If this fit succeeded, we could not conclusively claim that the changes in $(\langle\varepsilon_2\rangle)$ were correlated with changes in the MRO of the films. For all values, the $J_+/J_0=39$ data could not be successfully matched to the $J_+/J_0=3$ data; the closest "fit" that was possible yielded a surface roughness layer difference of 6 Å, a void difference of 4%, and no oxide layer, with a clearly visible difference in the spectra still remaining. This indicates that the ion bombardment may have both smoothed and slightly densified the film—effects which are consistent with changes observed in previous work on polycrystalline Si.[6] The remaining differences between the curves after fitting must therefore be the minimum due to the dielectric response changes between the films.

We have observed a direct correlation between MRO and low-energy ion bombardment of a-Si as measured with FEM. We believe ion bombardment alters the a-Si growth process at the surface, producing either a higher number, larger size, or more structurally ordered paracrystallites. Small variations in the vibrational and electronic densities of states have been detected by Raman scattering and SE. Although the changes are small, they correlate with the measurements of MRO by FEM, and so these techniques may prove to be additional tools in further studies of MRO and the paracrystalline structure. The hypothesis of low-energy ion bombardment enhancing the adatom mobility during growth is consistent with both the measured paracrystallite structure variations and the closest-fit SE parameters.

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