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Structural characterization of thin amorphous Si films

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Abstract

We present a study of structural changes occurring in thin amorphous silicon (a-Si). The a-Si films were deposited on single-crystalline Si substrates held at room temperature or 200 °C by magnetron sputtering of a Si target in pure Ar atmosphere, and therefore the films were hydrogen-free. All samples were annealed in vacuum and subsequently studied by EPR and GISAXS. A strong decrease in the dangling bonds content at lower annealing temperatures, and then an increase of it at around 550 °C, suggested significant structural changes. In parallel the samples were studied by GISAXS which confirmed changes at the nanometric scale attributed to voids in the material. A nice correlation of the results of the two techniques shows advantages of this approach in the analysis of structural changes in a-Si material.

Keywords: Amorphous silicon; Nanostructures; Small angle X-ray scattering; Electron paramagnetic resonance

1. Introduction

The intrinsic morphology of pure amorphous silicon (a-Si) on a nanometric scale has been an intriguing issue for more than two decades. This is mainly due to the fact that the actual morphology depends on several parameters such as: the method of preparation and the thermal history of a particular sample, as well as on many other structural properties [1–4]. It is known that a-Si deposited either by vacuum evaporation or sputtering almost inevitably contains nm-sized voids, which may or may not be connected. The existence of such structures within the a-Si has been confirmed by electron diffraction [5] and has been inferred from clustering of dangling bonds [2]. Still structural changes in a-Si during the course of thermal annealing are not completely characterized especially since the starting structure of a-Si is very much dependent on the preparation conditions. Different techniques are employed for such studies and one of them – electron paramagnetic resonance (EPR) – describes very well the changes during annealing [6,7]. Dangling bonds as a spin probe in the lattice provide very useful information on relaxation and structural changes. As they represent defects in the structure, these defects may act as the hopping sites for a variable range hopping conductivity, which is of interest as a phenomenon of disordered semiconductors. Moreover, such studies are of interest to understand if and how impurities, if present in the bulk, affect the structural changes evolving upon thermal treatment.

However, not all unsaturated bonds are paramagnetically active, and therefore we shall complement such information with structural measurements performed with grazing incidence small-angle X-ray scattering (GISAXS). The small-angle X-ray scattering (SAXS) technique is a well established technique for the detection of void distribution in a-Si and it has been applied with success to both a-Si and a-Si:H [8,9].

2. Experimental

Intrinsic amorphous silicon thin films were deposited onto single-crystalline Si (100) Czochralski wafers by rf magnetron sputtering in a CMS18 sputtering system (Kurt J. Lesker Co., Clairton, PA, USA). During deposition, the substrate holder rotated at 10 RPM in order to avoid the formation of a built-in stress preferential direction. The base pressure in the process chamber was 10^{-6}–10^{-5} Pa, and the working gas was argon of

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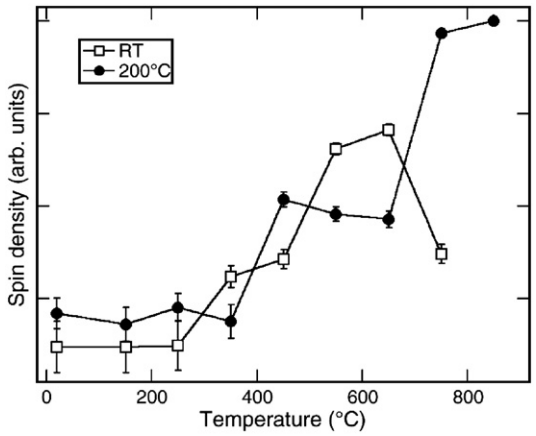

Fig. 1. Spin density versus annealing temperature of a-Si films deposited on substrates held at room temperature (open squares) or at 200 °C (black dots), respectively. After deposition, each sample was divided into several pieces, which were then annealed each at only one fixed temperature for 1 h in vacuum. Thus the data points shown were collected on different sample pieces (see also Experimental section).

5 N purity in a continuous flow. The working pressure during the deposition was 1.3 Pa and an ultrapure Si target (99.9999%) of 75 mm in diameter was used. The deposition rate was about 4 nm/min at 250 W rf magnetron power, and the final film thickness was about 1000 nm. During the deposition the substrate was held at a floating potential, and either at room temperature (RT) or at 200 °C. After the deposition, the samples were divided into several pieces. Each piece was then annealed in vacuum at a selected fix temperature for 1 h, and then cooled and measured at RT.

EPR measurements were performed employing a Varian E-109 spectrometer operating in the X-band (9.4 GHz). Several EPR were recorded in steps of 10° of the rotation of the magnetic field with respect to the Si (011) plane in order to reveal the dependence of the paramagnetic centers on the magnetic field orientation. In order to improve the signal-to-noise ratio, signal averaging (≈10 traces) was applied. The exact position of the *g*-factor and quantitative spin concentration was determined according to DPPH standard, and the detection limit of 10^{11} spins/cm^3 was achieved.

The GISAXS experiments were carried out at the synchrotron facilities of Elettra, Trieste, Italy at the SAXS beamline [10], using synchrotron radiation with wavelength $\lambda = 0.154$ nm (photon energy of 8 keV). The grazing angle of incidence was selected in the range $0.3° < \alpha_i < 1.4°$ for which the effective area of the beam foot print was smaller than the sample surface area (20 mm × 20 mm); and the grazing angle α_i was larger than the critical angle for total external reflection on the silicon substrate $\alpha_{crit}(Si) = 0.23°$. A two-dimensional CCD detector with 1024 × 1024 pixels, positioned perpendicular to the incident beam at a detector to sample distance $L = 2000$ mm, was used to record the SAXS intensity. A thin Al-strip was placed in front of the 2D detector to avoid its saturation in the specular plane direction where the usually much stronger surface scattering is present. The spectra were corrected for background intensity and detector response.

3. Results and discussion

Fig. 1 shows the variation of the spin density as a function of the annealing temperature for samples deposited either at RT or at 200 °C. As shown in the figure the spin density does not vary much until about 250 °C for the sample deposited at RT, or until about 350 °C for the sample deposited at 200 °C. For the sample deposited at RT annealing at temperatures above 250 °C produced a monotone increase in the spin density which passes through a maximum for annealing between 600 and 700 °C where it decreases again. On the other hand the spin density for the sample deposited at 200 °C increases strongly for annealing temperatures in the range 350–450 °C. Then it decreases slightly until about 650 °C, after which it increases again strongly for higher temperatures. A similar behavior was observed by Brodsky et al. [11], and they explained their results with cracking of newly formed crystals. In our case this increase in spin density upon high temperature annealing is however, much more pronounced. Due to a specific method of deposition, i.e. magnetron sputtering it is very likely that our material is loaded with voids that might coalesce at higher temperatures. Moreover, since it has been shown that at about 600 °C crystallization occurs [11] it is very likely that we are observing nanocrystals formation at even somewhat lower temperatures. These nanocrystals increase in number and size upon annealing at higher temperatures. Unlike our results, the results of Thomas et al. [6] show a continuous decrease of the spin density upon annealing up to 600 °C where it vanishes completely.

In order to verify this behavior of film inhomogeneity we have employed GISAXS which is very sensitive to density variations in the nanometer size range. As a typical result, Fig. 2 shows a GISAXS pattern obtained on a non-annealed sample, deposited at room temperature. Apart from the rather strong contribution of the surface scattering that is present in the vicinity of the specular plain ($q_y = 0$), there is a diffuse,

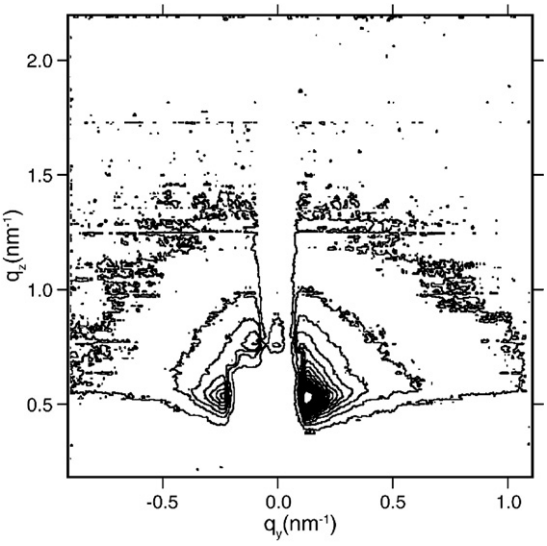

Fig. 2. Contour plot of GISAXS pattern obtained from a non-annealed sample, deposited at room temperature. The central vertical stripe is due to a thin, partly transparent Al-absorber in front of the 2D detector used to avoid its saturation.