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The structural ordering of thin silicon films at the amorphous to nano-crystalline phase transition by GISAXS and Raman spectroscopy

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Abstract

Thin silicon films were deposited by the plasma-enhanced chemical vapour deposition method using microwave (MW) and standard radio frequency (RF) gas discharge in silane gas diluted by hydrogen in the range that produces a mixture of amorphous and crystalline phases. The samples were analysed by Raman spectroscopy and grazing incidence small-angle X-ray scattering (GISAXS), while the threshold for the transition between the amorphous and crystalline phase was checked by the change in electrical conductivity. The crystalline fraction, estimated by Raman spectroscopy, varied between 0% and 70% while the individual crystal sizes were between 3 and 9 nm. However, the size distribution was broad suggesting also the existence of smaller and larger crystals.

The ''particles'' observed by GISAXS, most probably voids, were in the range between 2 and 12 nm. The voids in samples deposited by MW plasma were larger when closer to the surface. Their shape indicated the formation of a columnar structure perpendicular to the surface, more pronounced at higher temperature. The samples deposited by RF plasma and low power had spherically symmetric ''particles'' with uniform size across the depth of the samples. An increase of the RF power resulted in the formation of a columnar structure parallel to the surface. The observed differences are discussed in relation to the difference in growing kinetics of the used deposition methods.

Keywords: Nanocrystalline silicon; GISAXS; Raman spectroscopy

1. Introduction

By lowering the crystal dimensions down to the nano-scale or to a completely amorphous structure, it is possible to change the optical, electrical and other properties of a material. The combination of different degrees of structural ordering in the same material offers a great potential for the creation of multilayer structures suitable for many opto-electronic applications, such as solar cells, fleet screens, photo transistors, etc. However, for any practical use, it is important to establish a plausible characterization procedure that permits to make the correlation between the film properties and the dimension of the nano-objects on the one hand, and the nano-structure and growing condition on the other hand. In the case of thin film silicon, small angle X-ray scattering (SAXS) has been successfully applied in confirming the crucial role of nano-structure in opto-electrical properties: light-induced degradation, diffusion of hydrogen, phase segregation, etc. [1–7].

In estimating the structural properties on the nano-scale, SAXS has an advantage with respect to microscopy because it gives a certain average over the material. However, since SAXS detects only the presence of the origin of scattering as an object with a density that differs from the average electron density of the material (''particles''), for complete analysis this technique has to be combined with other methods.

In this paper, we study the nano-structural properties of thin films consisting of a mixture of amorphous and nano-crystalline phases, deposited by the plasma-enhanced chemical vapour deposition (PECVD) method by widely

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used radio frequency (RF) excitation and a new, very promising microwave (MW) excitation. The deposition conditions were selected to produce "typical" specimens to represent each of these deposition methods, in order to test the possibility of structural analysis combining grazing incidence small angle X-ray scattering (GISAXS) with vibrational and optical spectroscopy. In particular, the possibility of depth analysis by GISAX at different grazing incidence angles will be demonstrated.

2. Experimental

Thin silicon films were deposited by MW and RF PECVD on glass substrate. The first method uses an MW linear source to promote discharge in a gas mixture consisting of Ar and H injected close to the source, and SiH_4, which is injected more remotely from the source and close to the substrate [8]. The relatively high MW power (resulting in high deposition rates in the range of 1 nm/s) and the low substrate temperature (between 175 and 300 °C) chosen for this experiment resulted in layers which were vulnerable to post-oxidation, indicating a significant porosity.

The deposition of samples using RF discharge (RF PECVD) was done in a capacitively coupled planar diode source. The silane was diluted by hydrogen in the range between 5% and 6% of silane in the gas mixture. The low substrate temperature and high pressure at low power was applied, with a deposition rate between 1 and 2 nm/min.

Raman spectra were recorded by using a computerized DILOR Z24 triple monochromator with a Coherent INNOVA 100 argon ion laser operating at the 514.5 nm line for excitation. The applied laser beam of 150 mW was altered into a line focus in order to reduce the heating of the sample during recording of the Raman spectra. The typical resolution was between 1 and 2 cm^{-1}. During the analysis of the Raman spectra, the ratio of the areas under corresponding transversal optical (TO) phonon peaks in Raman was taken as a measure of the crystal to amorphous fraction. In the fitting procedure, the contribution of the amorphous phase to the Raman signal was estimated using the four Gaussian-like peaks for amorphous and two Voight-like for crystalline phases. The peak widths and frequency shifts were allowed to vary. This approach resulted in a variation of the peak positions depending on the degree of crystallinity. The crystalline TO peak position, ω_{TO}, was taken as an estimation of the crystal size using the formula [9]

$$d_{RAMAN} = 2\pi\left(\frac{2}{522-\omega_{TO}}\right)^{1/2}, \quad (1)$$

where d_{RAMAN} is the size of crystal in nanometre and ω_{TO} is measured in cm^{-1}.

The refraction index was calculated from the transmittance and reflectance measurements in the near-IR part of the spectra, while its value for the long wavelength was estimated according to the Wemple–Didomenico model [10,11].

GISAXS measurements were performed at the synchrotron ELETTRA, Trieste (Italy), at the SAXS beam-line [12], using an X-ray beam energy of 8 keV ($\lambda = 0.154$ nm). The samples were mounted on a stepping-motor-controlled tilting stage with a step resolution of 10^{-3} deg. The grazing angle of incidence was selected in the range $0.4° < \alpha < 1.4°$. X-ray scattering intensity pattern was acquired by a 2D position-sensitive CCD detector-at-a detector to sample distance $L = 2000$ mm. By changing the grazing angle, it is possible to obtain the depth distribution of the particles size. However, for obtaining exact values, the analysis is very demanding and time consuming, since the contribution to the scattered intensity at a certain angle comes from different depths. However, for a rough estimation, the dominant contribution to the lowest angles used in this experiment comes from the near-surface layer while the highest angles reveal the dominant contribution of a layer, some 300–400 nm in depth. The "particle size" in direction parallel to surface and perpendicular to it was estimated by using the Guinier approximation in the analysis of the 1D intensity distribution in two characteristic directions, parallel and perpendicular to the surface [13].

3. Results and discussion

The transition region between crystalline and amorphous phase appears for both applied deposition methods when using a high hydrogen dilution, between 5% and 10% of silane in the working gas. As illustrated in Fig. 1, for the MW plasma, the conductivity changes drastically in the threshold region (denoted by two lines). In the same region, a certain area under the crystalline TO peak in the Raman spectra becomes measurable. An increase of the applied power and/or temperature changes the degree of the crystalline to amorphous phase fraction.

The values of the refraction index of the deposited samples are plotted in Fig. 2 as a function of the crystal fraction. The dotted line in Fig. 2 represents the values expected for "voids-free" samples. Those values are well above all of the measured values, which indicate a films porosity rather than a surface roughness. The results show that the growth for MW-plasma samples is somewhat too fast for the given combination of substrate temperature and plasma conditions and the increase of crystal fraction is accompanied with higher porosity of the sample. The RF-plasma samples are more dense (refraction indexes are closer to "voids-free" values) indicating more homogeneous growth.

The possibility of growing thin film Si with crystal fraction independent of nano-crystal size has a great advantage for possible application, since for nano-crystals, the size defines opto-electrical properties. This is through for samples deposited by MW plasma and growing conditions used here: the sizes of crystals are not affected by the crystal fraction, as can be seen from Fig. 3 (open