Structure of plasma-deposited polymorphous silicon

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Abstract

The structure of plasma-deposited polymorphous silicon (pm-Si:H) films is studied by high resolution electron microscopy (HREM). The observation of epitaxy on crystalline silicon substrates suggests that polymorphous films are deposited under conditions close to equilibrium. Moreover, digital image processing and evaluation of electron micrographs indicate the presence of small crystallites and demonstrate an improved order in the amorphous silicon-like matrix when the pressure during deposition is increased. This is opposite to the decrease in the crystalline fraction deduced from the analysis of the dielectric function measured by spectroscopic ellipsometry (SE) and suggest that rather than the presence of crystallites, the main feature of polymorphous films is the achievement of a relaxed structure with some medium range order (MRO). The results are discussed with respect to the mechanism of pm-Si:H growth. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymorphous silicon (pm-Si:H) is a nanostructured material produced under plasma conditions where silicon clusters and/or nanocrystallites contribute to growth [1]. In our previous growth studies [2,3] we have already shown that this material is clearly different from protocrystalline and microcrystalline ($\mu\text{c-Si:H}$) silicon. Indeed, while the structure of the protocrystalline silicon continuously changes during deposition to become $\mu\text{c-Si:H}$, pm-Si:H films have been grown up to 10 μm in

thickness without changes in the film structure. However, a clear picture of the structure of silicon films produced at the edge of the microcrystalline transition [4] is lacking. Indeed, the study of the structure of non-crystalline materials a delicate subject and demands accuracy and caution. So far, high resolution electron microscopy (HREM) investigations have been mostly performed to demonstrate the presence of crystallites in pm-Si:H films. By contrast, fluctuation electron microscopy has been suggested as a powerful technique to study medium range order (MRO) [5].

In this study we address the question of quantifying the size and fraction of crystallites in the pm-Si:H matrix, and their connection to improved transport properties of the material [6]. To this end, we focus on the analysis of the non-crystalline part of pm-Si:H images obtained by HREM and

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Table 1

Effect of the total pressure during deposition on the deposition rate and composition of silicon films

Reference	Pressure (Pa)	r_d (Å/s)	%H	%Crist.	%Void
010043	240	2.49	15	0	0
010042	213	1.85	13	0	0.5
010036	187	1.84	14.5	8	1
010033	93	1.06	18	13	3.7
010024	80	1.04	19	15	5.5
010023	67	1.04	25	23	4.5

compare them to those of a-Si:H and μ c-Si:H. The HREM results are discussed with respect to the information on the film structure deduced from conventional techniques such as SE, infrared absorption, hydrogen evolution and nuclear analysis.

2. Experiments

A series of samples was deposited on different substrates by the dissociation of a 2% silane in hydrogen mixture at 250 °C by the standard radio frequency glow discharge technique [7] under an RF power of 90 mW/cm². The total gas pressure was varied between 53 and 240 Pa (see Table 1). At pressures lower than 90 Pa, the films were μ c-Si:H. At higher pressures there is a change in the discharge regime, which results in a different plasma chemistry leading to the formation of large silicon clusters and silicon crystallites (up to 2 nm in radius), and to the growth of pm-Si:H films. Standard a-Si:H was also produced by the dissociation of pure silane at low pressure and low RF power.

Cross-sections of the samples deposited on crystalline silicon were also prepared for HREM observation in a JEM 4010 microscope operating at 400 kV. Micrographs were recorded using optimum imaging conditions (near Scherzer defocus) and were subjected to digital image processing and evaluation. The degree of positional order in the micrographs was then numerically analyzed, calculating their Fourier transform (FT) and autocorrelation function.

The dielectric function of the films was obtained by SE, and analyzed by a combination of the tetrahedron model and the Bruggeman effective medium approximation. This analysis allowed

quantification of the hydrogen content as well as the crystalline and void fraction of the films. The validity of the ellipsometry modelling was checked against the hydrogen content deduced from elastic recoil detection analysis (ERDA) and the films density from Rutherford backscattering (RBS) measurements [8].

3. Results

3.1. HREM

Fig. 1 shows an overview of a cross-sectional HRTEM micrograph of the standard amorphous and the polymorphous sample deposited at 240 Pa. In the micrograph, both the film and the interface with the crystalline substrate are shown. In the case of a-Si:H, there is a sharp interface between the crystalline substrate and the amorphous layer. That is not the case for pm-Si:H, where some epitaxial crystallites of sizes between 4 and 13 nm are seen near the interface to the substrate. Concerning the bulk film itself, it has an amorphous aspect for both samples and apparently no crystallites can be found. Therefore, a more accurate analysis is required to compare both kinds of matrix. To this aim, we utilized two different calculations: (i) the FT and (ii) the autocorrelation function.

The two-dimensional FT gives a measure of the mean spacings of image features. It should consist of continuous circular bright rings, the width of which gives a measure of the dispersion of these spacings. In this sense we may conclude, the broader the rings are, the more disordered is the material. As an example, Fig. 2(a) shows the

Fig. 1. Cross-sectional HREM micrographs: (a) hydrogenated polymorphous (b) hydrogenated amorphous silicon. In both cases the films have been deposited on crystalline silicon.

profile of the FT calculated from micrographs of amorphous and polymorphous silicon (240 Pa). The FT ring width corresponding to a-Si:H is clearly larger than that corresponding to pm-Si:H, indicating that pm-Si:H exhibits more positional order. The width of the FT rings is plotted in Fig. 2(b) for a variety of films as a function of the total pressure applied during film deposition. The tendency is clear: under otherwise equal conditions, increasing pressure results in a decreasing FT ring width and thus, a material with improved MRO.

Another way of analyzing the content of HREM images of amorphous specimens is to de-

Fig. 2. Profile of the intensity of the FT of the amorphous-like zone of the micrographs (a) and half width at half maximum of the intensity of the FT as a function of the total gas pressure (b).

termine their autocorrelation function. The autocorrelation function

$$A(x, y) = \int_{-\infty}^{+\infty} \left\{ \int_{-\infty}^{+\infty} f(x, y) e^{-i2\pi(ux+vy)} dx dy \right. \\ \left. \times \int_{-\infty}^{+\infty} f(X_0, Y_0) e^{-i2\pi(ux_0+vy_0)} dX_0 dY_0 \right\} \\ \times e^{i2\pi(ux+vy)} du dv$$

applied to the two-dimensional intensity function $f(x, y)$ of the image is a discrete two-dimensional function reflecting the average correlation between

image features separated by a certain distance $\vec{r} = (x, y)$. As in the image of a completely random object there are no preferred directions, the autocorrelation function must have rotational symmetry with the origin (0,0) at the center. Application of the autocorrelation function is useful for detecting the degree of order of an image submerged by amorphous ‘noise’. In fact, it contains the same information as the FT, but visualized in real space, and may be interpreted in a more intuitive way. Fig. 3 shows the autocorrelation functions calculated from micrographs of the a-Si:H sample (a), the pm-Si:H sample deposited at 214 Pa (b) and the pm-Si:H sample obtained at 240 Pa (c). The two-dimensional autocorrelation function consists of some rings centered around the origin (0,0), the extension of which gives a measure of positional order hidden in the contrast features of the matrix. As seen in Fig. 3, clearly more rings appear in the autocorrelation of the pm-Si:H sample deposited at the highest pressure. In the case of pm-Si:H one can also recognize a certain texture of the rings. Moreover, in the case of the pm-Si:H deposited at 213 Pa, the rings have a kind of polygonal aspect. The distance between the rings is 3.1 Å, corresponding to the interplanar spacing of $\langle 111 \rangle$ in c-Si. These peculiarities can be considered as signatures of translational order due to crystal-like ordering.

3.2. SE

The dielectric function of the thin films was obtained by the analysis of SE measurements using the Tauc–Lorentz dispersion law [9]. The results are shown in Fig. 4 for the pressure series, along with the spectra of a-Si:H and polycrystalline silicon (p-Si). For simplicity, only the imaginary part of the dielectric function, ϵ_{im} , is plotted. Except for the p-Si, all the ϵ_{im} show a similar aspect. They consist of a band, centered between 3.5 and 3.75 eV. As shown in Table 1, the films deposited at pressures higher than 93 Pa are polymorphous, while at lower pressures they are microcrystalline. The transition from $\mu\text{c-Si:H}$ to pm-Si:H is not sharp and cannot be accounted for the disparition

Fig. 3. Two-dimensional autocorrelation function of the amorphous-like zone of the micrographs shown in Fig. 1 for a standard hydrogenated amorphous silicon (a), a hydrogenated polymorphous silicon prepared at 213 Pa (b), and a hydrogenated polymorphous silicon prepared at 240 Pa (c).

Fig. 4. Imaginary part of the dielectric function for different materials. The references: in (□) for crystalline silicon (with 10% voids to reduce the values of epsilon), and in (—) a for a dense hydrogenated amorphous silicon. The materials corresponding to the pressure series are represented by: (◆) 240, (○) 213 Pa, (▼) 187 Pa, (···) 93 Pa, and (■) 80 Pa.

of the crystalline phase. Indeed, some crystallites are often observed in pm-Si:H films deposited at low pressure range. Nevertheless, the transition is supported by the improvement of the order of the silicon matrix as shown in Fig. 2(b). In the case of a-Si:H, the center of the band is at 3.5 eV, while for pm-Si:H the center is shifted 0.15 eV to higher energies. As may be seen in the figure, this shift is more pronounced in the case of the sample deposited at 80 Pa. ϵ_{im} of p-Si shows a completely different aspect. First, the edge is shifted to much higher energies, and second it exhibits two shoulders at 3.5 and 4.2 eV. The shift of ϵ_{im} to higher energies can be due to the presence of a small crystalline fraction, but also to a higher hydrogen content in the sample. Therefore, an accurate modelling of the dielectric function is needed, to understand the origin of the changes in ϵ_{im} of pm-Si:H and μ c-Si:H with respect to a-Si:H. We recently applied a combination of the Bruggemann effective medium approximation and the tetrahedron model to analyze the dielectric function of various types of amorphous and pm-Si:H films. In this way, the hydrogen content and void fraction could be quantified and small crystalline fractions between 5–20% were detected [8].

The results of the corresponding SE analysis, hydrogen content, void and crystalline fraction, are shown in Table 1. pm-Si:H films deposited at high pressure are characterized by a high hydrogen content (15%) and negligible void fraction. This latter result is confirmed by the high values of their mass density [10], and it is a remarkable result, because usually in a-Si:H a high hydrogen content matches with a low mass density.

As shown in Table 1, μ c-Si:H samples, deposited at 80 and 93 Pa, have a value of crystalline fraction of 15% and 13%, respectively. As the pressure increases and the material changes to pm-Si:H, the crystalline fraction continues to decrease down to 8% at 187 Pa and is not detectable at higher pressure. But the origin of the crystalline fraction is in both cases completely different and that is why we have different names. In μ c-Si:H, the nucleation takes place in the thin film itself and the crystalline fraction increases during growth, i.e., with thickness. On the contrary, the crystalline fraction of 8% in the pm-Si film is homogeneous through the layer. This is caused by different growth mechanisms of μ c-Si:H and pm-Si:H as discussed elsewhere [3].

4. Discussion

The formation of an epitaxial layer at the interface to the crystalline substrate in the case of pm-Si:H deposition (Fig. 1) can be related to the growth conditions of the material. Indeed, pm-Si:H is deposited under high hydrogen dilution which enhances the mobility of the precursor species arriving at the surface and allowing them to find a more stable position and grow a more ordered material. However, it is interesting to note that the thickness of the epitaxial layer is about the same for all films presented in Table 1 despite of the increase in deposition rate by more than a factor of 2 which should result in a decrease of the epitaxial thickness [11].

The occurrence of an epitaxial layer thus indicates that pm-Si:H films are produced under plasma conditions close to equilibrium, and thus one may expect an improved order in the amorphous-like matrix. It is a matter of fact that

imaging of silicon nanocrystallites in a silicon amorphous matrix is not a simple task. Indeed, the specimens have to be very thin and the nanocrystallites well oriented, with respect to the electron beam. Moreover, it is known that ion beam milling, applied for cross-section preparation, may cause some structural deterioration of the film. Therefore, the evaluation of autocorrelation function graphs can help to rate the extent of positional order in the amorphous matrix. The results shown in Fig. 3 give a clear indication of an improved order when going from a-Si:H to pm-Si:H films deposited at high pressure. They are in agreement with the FT analysis shown in Fig. 2(b). Moreover, the maximal order was obtained for material deposited at the highest pressure (240 Pa). In fact, this material has also shown the best electronic properties. This means that the improvement of the MRO is related to the improvement of the electronic properties.

To support our interpretation of the autocorrelation function procedure we also did some estimation by means of model images created by numerical superposition of images of amorphous silicon and of silicon nanocrystallites of appropriate size and concentration. Reasonable results obtained for 2 nm size and 2–3% crystalline fraction confirm this method as being useful in studies like the present one.

5. Conclusion

We have studied the local structure of pm-Si:H and a-Si:H thin films by an accurate analysis of HRTEM micrographs combined with macroscopic properties from a detailed analysis of the dielectric function. A homogeneous distribution of crystallites through the layer for crystalline fractions down to 8% has been demonstrated by SE.

Even lower values (down to 2%) have been deduced from the modeling of the autocorrelation function of HREM images. Above all, it appears that the most important feature of pm-Si:H films is the improved order in their amorphous-like matrix. In our opinion, it is the improved order which is the basis of the excellent electronic and transport properties of pm-Si:H films.

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References

- [1] P. Roca i Cabarrocas, *J. Non-Cryst. Solids* 266–269 (2000) 31.
- [2] E.A.G. Hamers, A. Fontcuberta i Morral, C. Niikura, R. Brenot, P. Roca i Cabarrocas, *J. Appl. Phys.* 88 (2000) 3674.
- [3] A. Fontcuberta i Morral, P. Roca i Cabarrocas, *Thin Solid Films* 383 (2001) 161.
- [4] S. Guha, J. Yang, D.L. Williamson, Y. Lubianiker, J.D. Cohen, A.H. Mahan, *Appl. Phys. Lett.* 74 (1999) 1860.
- [5] P.M. Voyles, J.E. Gerbi, M.M.J. Treacy, J.M. Gibson, J.R. Abelson, *Phys. Rev. Lett.*
- [6] J.P. Kleider, C. Longeaud, M. Gauthier, M. Meaudre, R. Meaudre, R. Butté, S. Vignoli, P. Roca i Cabarrocas, *Appl. Phys. Lett.* 75 (1999) 3351.
- [7] P. Roca i Cabarrocas, J.B. Chévrier, J. Huc, A. Lloret, J.Y. Parey, J.P.M. Schmitt, *J. Vac. Sci. Technol. A* 9 (1991) 2331.
- [8] A. Fontcuberta i Morral, P. Roca i Cabarrocas, to be published.
- [9] G.E. Jellison Jr., F.A. Modine, *Appl. Phys. Lett.* 69 (1996) 371.
- [10] S. Vignoli et al., these Proceedings, p. 220.
- [11] J. Thiesen, H.M. Branz, R.S. Crandall, *Appl. Phys. Lett.* 77 (2000) 3598.