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Control of crystallinity of microcrystalline silicon film grown on insulating glass substrates

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Abstract

The amorphous incubation layer commonly found in microcrystalline silicon (μc-Si:H) grown on insulating glass substrates by plasma-enhanced chemical vapor deposition has been successfully eliminated simply by dilution of the SiH_4 to a SiH_4/H_2 flow ratio $< 1/99$. Using an amorphous layer free μc-Si:H as a seed an epitaxial-like growth of μc-Si:H was obtained. It is shown that, with the seeded growth scheme, one can grow amorphous layer free thin μc-Si:H films and control the crystallinity of the films with relative ease. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Microcrystalline silicon; Plasma-enhanced chemical vapor deposition

1. Introduction

Microcrystalline silicon (μc-Si:H) was first prepared at low temperatures (< 400 °C) by plasma-enhanced chemical vapor deposition (PECVD) nearly 20 years ago [1]. However, it has been a challenge to control the crystallinity of very thin (< 50 nm) Si films grown on electrically insulating glass substrates such as Corning 7059 glass and fused quartz (silica). The difficulty arises from the fact that a layer of the film right on top of the glass substrate is amorphous even though the rest of the film may exhibit a high crystallinity [2–5]. The reported values for the thickness of this initial amorphous layer (also sometimes termed the incubation layer) are > 10 nm. In this paper, we report on the successful elimination of the amorphous incubation layer in PECVD growth of μc-Si:H. We show that, with a triode PECVD system [6], H_2 dilution of the SiH_4 gas provides a simple and effective way to control the structure of very thin Si:H films on insulating glass substrates.

2. Experimental details

The triode PECVD system used in this work was operated at 13.56 MHz. The substrate holder was grounded. The substrates were fused quartz and were cleaned using the SC-1 solution (H_2O:31%H_2O_2:28%NH_4OH = 5:1:1, 80°C). The reactant gas was SiH_4 diluted in H_2. The flow rates

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of SiH_4 and H_2 were such that the total flow rate was ~ 100 sccm, and the SiH_4/H_2 flow ratio was varied down to 0.33/99. A Pd-film H_2 purifier was used to purify the H_2 gas. The ratio of the SiH_4 partial pressure to that of H_2 in the chamber was larger than the SiH_4/H_2 flow ratio, due to a slower evacuation speed for SiH_4 of the pumping system. The deposition parameters are as follows. Substrate temperature: 250°C; rf power density: ~ 1 W/cm^2; chamber pressure: 6.65 Pa; mesh bias: -100 V. The base pressure of the chamber was $\sim 4 \times 10^{-6}$ Pa at room temperature. A shutter was placed right above the substrate during the adjustment of the plasma following ignition. The crystallinity of the films was determined using Raman back scattering excited with a He–Ne laser.

3. Results

Apparently, the key to controlling the crystallinity of very thin films is to eliminate the amorphous incubation layer. To this end, we tried depositions with SiH_4/H_2 flow ratios (R) down to 0.33/99. It is found that with decreasing R, the crystallinity of the film improved [7]. In particular, we find that with $R = 0.33/99$, the film is of high crystallinity even when the thickness is ~ 10 nm. Fig. 1 shows the Raman spectra for two films grown with $R = 0.33/99$. The thicknesses of the two films were not directly measured and were estimated from the deposition rate for thicker films, but confirmed by transmission electron microscopic (TEM) measurement. As one can see from Fig. 1, the crystallinity remains high ($\sim 90\%$) at 12 nm. At a film thickness of 6 nm, however, the broad shoulder (at ~ 480 cm^{-1}) in the Raman spectrum increased, indicative of an increased amorphous phase fraction. Nevertheless, the spectrum is clearly still dominated by the crystal band at ~ 520 cm^{-1}. Unfortunately, for films thinner than 6 nm, a reliable Raman measurement was no longer possible, due to an increased influence of the signal from the substrate. However, the high resolution TEM cross-sectional view of a related sample reveals that at a SiH_4/H_2 flow ratio of 0.33/99 under the present deposition conditions, crystal grains start to form essentially right from the substrate, with an incubation layer of less than 1 nm. Therefore, we have effectively eliminated the initial amorphous layer in μc-Si:H growth simply by using high H_2 dilution of SiH_4.

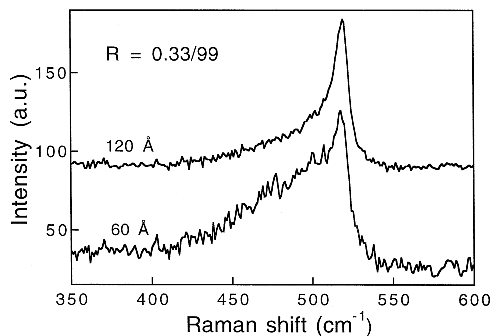

Fig. 1. Raman spectra for two Si:H films deposited at a SiH_4/H_2 flow ratio of $R = 0.33/99$. The film thicknesses are given in the figure.

One drawback of high H_2 dilution is that it results in a lower deposition rate. To speed up the deposition, low H_2 dilution is desirable. An interesting question to ask is, if one increases R after the deposition of an ultrathin layer with a much smaller R (say 0.33/99) will the structure of this ultrathin layer be carried on during the growth that follows? The answer to the above question is important not only from the viewpoint of applications but from the viewpoint of material science in general. Such a growth scheme is termed seeded growth and the initial ultrathin layer is called the seed layer [7]. The effect of the seed layer on the crystallinity of the film is shown in Fig. 2. The seed layer in Fig. 2 was deposited with $R = 0.33/99$ and the gas flow ratio for the subsequent growth was either $R = 1.2/99$ (lower two spectra) or $R = 3.2/97$ (upper two spectra). The thickness of the seed layer is given in the parentheses and the total film thickness is ~ 40 nm for $R = 1.2/99$ and 53 nm for $R = 3.2/97$. One can see that, for both gas flow ratios the use of a seed layer improves the crystallinity of the film. In fact, even with a 2 nm thick seed layer improvement of the crystallinity has been obtained [7].

Thus far, we have implicitly assumed that the seed layer is a proper layer, i.e., having a well defined thickness. However, this assumption is not guaranteed for an ultrathin layer. In the worst case, the ‘layer’ would consist of spatially well-separated

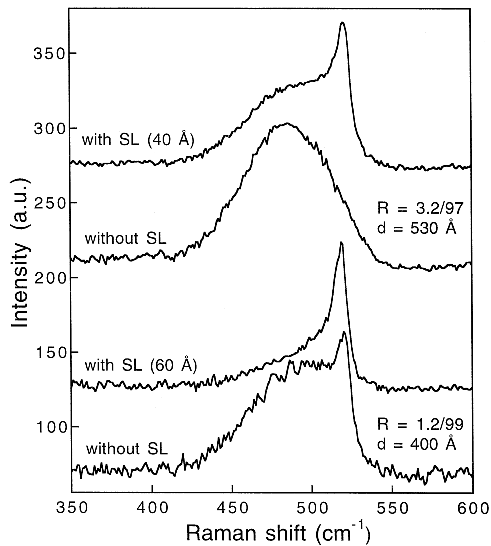

Fig. 2. Raman spectra for Si:H films grown with or without a seed layer (SL). The lower two films are for $R = 1.2/99$ and are 400 Å thick. The upper two films are for $R = 3.2/97$ and are 530 Å thick. The seed layer was deposited with $R = 0.33/99$ and its thickness is given in the parentheses.

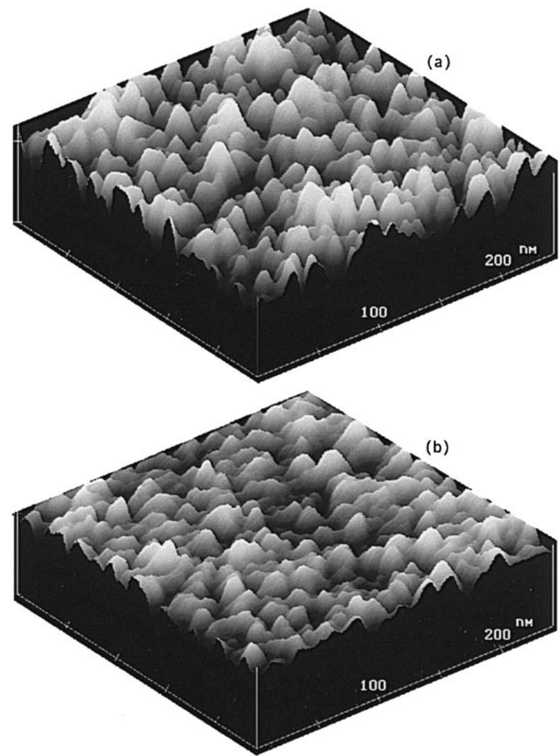

Fig. 3. Topographies of two 20 Å thick films. (a) Deposited with $R = 0.33/99$. (b) Deposited with $R = 1.2/99$. The height of the vertical bar is 4 nm.

pillars whose heights are in excess of the nominal thickness of the layer. To gain more insights into the seed layer, we carried out atomic force microscopic (AFM) measurement on two 2 nm thick films deposited, respectively, with $R = 0.33/99$ (Film 1) and $R = 1.2/99$ (Film 2). Fig. 3 shows the topographies of the two films. Clearly, Film 1 (Fig. 3a) is rougher than Film 2 (Fig. 3b). For the entire scanned area (400×400 nm^2), the root-mean-square (RMS) surface roughness is 0.56 nm for Film 1 and 0.35 nm for Film 2. On the other hand, we do not see much difference between the feature (island) densities of the two films and the feature density is $\sim 2 \times 10^{11}$ cm^{-2}. Judging from the crystallinity of thicker films deposited with $R = 1.2/99$, Film 2 is most certainly amorphous. Thus, the larger surface roughness of Film 1 indicates that this film contains sufficient fraction of crystal grains, which is consistent with the TEM result. It is important to note, however, that, even without taking into account the contribution from the roughness of the substrate (which is 0.28 nm), the average peak-valley vertical distance for Film 1 is only 1 nm (half of the nominal film thickness). These results suggest that the seed layer (deposited with $R = 0.33/99$) is reasonably flat and that, perhaps, coalescence has already started at a thickness of 2 nm.

4. Discussion

We have seen that H_2 dilution is essential for eliminating the amorphous incubation layer. Thus one might think that nucleation of crystallites on glass is controlled only by the gas phase. While the gas phase chemistry is undoubtedly important, we stress here that the physical and chemical properties of the substrate surface also play a crucial role in determining the structure of very thin films. We have found that the crystallinity of the film depends on the chemical treatment of the substrate.

Next, we discuss how the seed layer can serve to improve the crystallinity of the film. There are two possibilities: (a) quasi-epitaxy and (b) secondary nucleation of crystallites. In (a), the structure of the

seed layer is important and, ideally, is exactly followed during the growth. For each grain, regardless of the orientation, the growth is epitaxial in the usual sense. In (b), however, the structure of the seed layer is not copied in the growth. Rather, the seed layer only provides a growth surface that enhances crystal nucleation. The TEM measurement of a film grown at $R = 1.2/99$ with a seed layer of 6 nm shows that there is no clear interface between the seed layer and the rest of the film; crystal grains formed in the seed layer continue to grow after the gas flow ratio is increased by nearly four times. These results indicate that quasi-epitaxial growth indeed takes place under the deposition conditions employed. This is not say, however, that secondary nucleation does not occur throughout the growth. In fact, as the growth proceeds, some of the grains will be terminated and secondary nucleation of crystallites must occur. Evidence for epitaxial-like growth has also been reported for polycrystalline Si [8].

Obviously, a key requirement on the seed layer is that it must be stable against the film growth conditions. In this sense, it is relevant to mention that a similar growth scheme has also been tried by Nguyen et al. [9] on Cr coated glass substrates, but with no success. Nguyen et al. prepared a seed layer 1 nm thick by atomic H etching of amorphous Si. However, they found that the seed layer was etched away when exposed to a SiH_4/H_2 plasma used in PECVD. In our approach, however, the seed is planted using the same growth mode as for the film growth but at a lower SiH_4/H_2 gas flow ratio (higher H_2 dilution). This ensures that the seed layer is not altered when exposed to the growth plasma. Another important feature of our approach is that the seed layer is relatively flat, in the sense that there are no features on the surface whose heights are larger than the nominal layer thickness. This suggests that the seeded growth scheme would find a wide range of applications in devices where very thin microcrystalline layers of well defined thicknesses are required.

5. Conclusions

The amorphous incubation layer commonly found in μc-Si:H grown on insulating glass substrates by PECVD has been successfully eliminated simply by H_2 dilution of the SiH_4 to a SiH_4/H_2 flow ratio well below 1/99. Using an ultrathin amorphous layer free μc-Si:H as a seed layer quasi-epitaxial growth of μc-Si:H was obtained. It is shown that, with the seeded growth scheme, one can grow amorphous layer free thin μc-Si:H films and control the crystallinity of the films with relative ease. The AFM observation of the seed layer shows that the surface of the seed layer is relative flat, indicating that the seeded growth scheme is well suited for applications in devices that require very thin microcrystalline layers of well-defined thicknesses.

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