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Letter to the Editor

Hydrogenated amorphous silicon with substrate-dependent structure

An Shih, Si-Chen Lee *

Department of Electrical Engineering, National Taiwan University, No. 1 SEC 4, Roosevelt Road, Taipei, Taiwan, ROC

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Abstract

Hydrogenated amorphous silicon (a-Si:H) thin films grown at 250°C on (1 0 0) crystalline substrate using plasma-enhanced chemical vapor deposition (PECVD) with SiH₄/H₂ gas flow ratio equal to 5/1 (sccm) are investigated by transmission electron microscopy. It is found that the thin film is totally amorphous when grown on a glass substrate. But when the substrate is changed to crystalline silicon, some crystalline grains are found embedded in the amorphous structure in certain regions even if the thickness of the film reaches 600 nm. It is suggested that the amorphous silicon film grown on a crystalline silicon substrate at a temperature of 250°C without heavy H₂ dilution is a mixed network of a small amount of crystalline silicon and the major portion of amorphous silicon. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The techniques commonly used to grow microcrystalline silicon (μc-Si:H) include chemical transport deposition [1,2], radio frequency glow discharge [3–10], sputtering [11], remote plasma deposition [12] and electron cyclotron resonance (ECR) [13]. Among these depositing techniques, glow discharge seems to be the most promising method for practical use because of its high throughput, good step coverage, simplicity and low cost. In order to grow μc-Si:H by glow discharge method, a few percent of SiH₄ diluted with H₂ or Ar is necessary [6–10]. Without heavy H₂ or Ar dilution, it is usually believed that the thin films grown have an amorphous structure, which is true

when the substrate is 7059 glass. Recently, Kondo et al. [6] reported that initially grown μc-Si:H layer by plasma-enhanced chemical vapor deposition (PECVD) strongly depends on the substrate type with the gas flow of SiH₄/H₂ equal to 1/49 (sccm). They reveal that the thin films grown on germanium, graphite and aluminum substrates exhibit a much stronger 520 cm⁻¹ Raman peak than those on sapphire, 7059 glass and quartz substrates. But when the substrate is replaced by crystalline silicon, the 520 cm⁻¹ peak cannot be distinguished from the huge substrate Raman peak. In this paper, we will show that in the normal hydrogenated amorphous silicon growth conditions by means of PECVD without heavy H₂ dilution, microcrystalline silicon grains still appear even if the thickness of the film reaches 600 nm. It is suggested that the amorphous silicon thin films grown by PECVD without heavy H₂ dilution have strong correlation with substrate and appear to be a mixed network

* Corresponding author. Tel.: +88-62 23 63 5251; fax: +88-62 23 67 5509.

of a small amount of crystalline silicon and the major portion of amorphous silicon when the substrate is crystalline silicon.

2. Experiment

The a-Si:H samples described in this paper are deposited by PECVD. The deposition parameters of the a-Si:H thin films are as follows: RF power density 0.11 W cm^{-2} , RF frequency 13.56 MHz, substrate temperature 250°C , chamber pressure 0.4 Torr, SiH_4 flow rate 5 sccm, H_2 flow rate 2 sccm and the growth rates 0.3 nm s^{-1} . The thickness of the samples for transmission electron microscopy (TEM) is 100 nm a-Si:H on 7059 glass and 600 nm on (1 0 0) c-Si, respectively. The TEM sample of a-Si:H on 7059 glass is prepared by diluted BOE selective etching, and on c-Si is prepared by ion milling. In order to prevent the film from crystallizing during the process of ion milling, liquid N_2 is used to cool the sample until the film is ion-milled to less than 100 nm. Furthermore, to keep the undesirable deposition of sputtered-off crystalline Si particles from landing on the pictured position, the thickness of the thin film is selected up to 600 nm and the film is processed by ion milling with a low angle from 8° to 10° . The film is not broken by ion milling in the pictured position.

3. Results and discussion

Fig. 1(a) shows the bright field image of a-Si:H deposited on 7059 glass. It is a pure amorphous glassy structure. Fig. 1(b) shows the diffraction pattern of Fig. 1(a). The first diffraction ring corresponds to the crystalline silicon (1 1 1) diffraction ring and the faint second ring appears between the corresponding (2 2 0) and (3 1 1) diffraction rings. The intensities of both rings are uniform. Most of a-Si:H deposited on c-Si also has the glassy structure and shows the same diffraction pattern as Fig. 1(b). But as shown in Fig. 2(a) the image of TEM bright field reveals that some crystalline grains are embedded in the amorphous structure in certain regions. Because these granules are clus-

(a)

(b)

Fig. 1. (a) TEM bright field picture of the a-Si:H film deposited on 7059 glass. (b) Diffraction pattern of (a).

tering instead of uniformly spreading in the amorphous network, it is difficult to estimate the fraction of crystalline grains. But because the 520 cm^{-1} peak in Raman spectra cannot be distinguished from the 480 cm^{-1} peak in this sample, the fraction of crystalline grains should be few. The size of the crystalline grains ranges from 30 to 200 nm. Fig. 2(b) displays the diffraction pattern of the region shown in Fig. 2(a). It is evident that two clear bright diffraction spots appearing on the second diffraction ring indicating the existence of the Si crystalline grains. The intensity of the second ring is not uniform, which suggests that preferential crystallization of silicon does occur. There is also a clear bright spot on the larger diffraction ring (as pointed by the arrow). Therefore, it is demonstrated that in the amorphous films,

(a)

(b)

Fig. 2. (a) TEM bright field picture of the a-Si:H film deposited on c-Si. (b) Diffraction pattern of (a).

clusters of the crystalline Si granules appear in the certain regions. There may be two possible mechanisms to explain this phenomenon. One is that during the initial growth, the structure in some regions may follow the trend of crystal silicon and form the crystalline structure. Once crystals form, subsequent growth will follow the trend established in these regions, so the microcrystalline grains will appear in clusters. The second possibility is that the crystalline grains appear when the grown films reach some critical thickness such that the accumulated stress favors the growth of crystalline grains.

4. Conclusion

In our deposition conditions, the grown film should be the amorphous structure when the substrate is 7059 glass as shown in Fig. 1(a). But when the substrate is changed from glass to c-Si, some crystalline grains appear. Therefore, the growth by PECVD highly depends on the type of the substrate. Even if the thickness reaches 600 nm, some crystalline grains appear in the films. This also supports the viewpoint of Kondo et al. [6] that different substrates induce different crystal grade when using PECVD.

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