

EFFECT OF SiF₄ ADDITION ON THE STRUCTURES OF SILICON FILMS DEPOSITED AT LOW TEMPERATURE BY REMOTE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Silicon films were deposited at 430 °C by remote plasma chemical vapor deposition (RPECVD) with a gas mixture of Si₂H₆/SiF₄/H₂. The silicon films deposited without and with SiF₄ were characterized using atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Both silicon films have the same rugged surface morphology, but, the silicon film deposited with SiF₄ exhibits more rugged. The silicon film deposited without SiF₄ is amorphous, whereas the silicon film deposited with SiF₄ is polycrystalline with very small needle-like grains which are perpendicular to the substrate and uniformly distributed in the thickness of the film. The silicon film deposited with SiF₄ was found to have a preferred orientation along the growth direction with the <110> of the film parallel to the <111> of the substrate. The effect of SiF₄ during RPECVD was discussed.

1. INTRODUCTION

Amorphous silicon (a-Si) thin film transistors (TFTs) using low temperature processes are currently applied towards addressing circuits of active matrix liquid crystal display (AMLCD). Because of the low mobility and on-current, a-Si TFTs are replaced by polycrystalline silicon (poly-Si) TFTs in driving circuits of AMLCDs (1). Since ordinary glass substrates can not endure high temperature (>600 °C) processing, the higher temperature would prohibit the integration of both a-Si and poly-Si TFTs on the same glass substrate (2). Therefore, low temperature deposition of poly-Si films becomes desirable for the integration of a-Si and poly-Si TFTs. However, at low temperature, it is relatively difficult to grow poly-Si films because adatom mobility is low and incorporation of impurities, especially oxygen and hydrogen, is more likely (2).

Recently, low temperature poly-Si growth has been reported using plasma enhanced chemical vapor deposition (PECVD) with a gas mixture of SiF₄/SiH₄/H₂ (3). In the previous work, we deposited poly-Si films with a gas mixture of Si₂H₆/SiF₄/H₂ at low temperature by remote plasma enhanced chemical vapor deposition (RPECVD) and studied the effects of SiF₄ flow rate and plasma power on deposition rate and crystallinity (4). In order to understand the nature of the effect of SiF₄, in the present paper, the structures of the silicon films deposited without and with SiF₄ at low temperature by RPECVD were studied using atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

2. EXPERIMENTAL

The silicon films were prepared by RPECVD with a gas mixture of Si₂H₆/SiF₄/H₂. Only the hydrogen was excited when it passed through the plasma region. A Si₂H₆ and SiF₄ mixture was

was introduced through the dispersal ring into the downstream of plasma without excitation. The Si (111) wafer with 100 nm thickness SiO_2 film, obtained from thermal oxidation at 1000 °C in a furnace, was used as a substrate. Deposition parameters were as follows: reactor pressure 400 mtorr, plasma power 60 W, deposition temperature 430 °C, deposition time 2 hours. For the silicon film deposited without SiF_4 , Si_2H_6 flow rate was 1 sccm and H_2 flow rate 100 sccm. For the silicon film deposited with SiF_4 , Si_2H_6 flow rate was 0.1 sccm, SiF_4 flow rate 20 sccm and H_2 flow rate 100 sccm.

The surface morphology of the deposited silicon films was observed using an Autoprobe-CP model atomic force microscope. Cross sectional specimens for transmission electron microscopy (TEM) were first glued face to face, cut, then ground, dimpled and thinned by ion milling. TEM observations were conducted using a JEOL JEM-200CX transmission electron microscope operating at 100 kV. The structures of the deposited films were analyzed using a Rigaku D-Max 1400 X-ray diffractometer with $\text{Cu K}\alpha$ radiation operating at 50 kV, 150 mA.

3. RESULTS AND DISCUSSION

Fig. 1 shows the three dimensional AFM images of the silicon films deposited without and with SiF_4 . As SiF_4 was added during deposition, the surface roughness increases from 1.4 nm for the silicon film deposited without SiF_4 to 1.6 nm for the silicon film deposited with SiF_4 . Compared with the silicon film deposited without SiF_4 , the silicon film deposited with SiF_4 exhibits more rugged surface morphology. The average diameter of the rugged mountains of the silicon film deposited without SiF_4 is about 160 nm, and that with SiF_4 about 140 nm. From the AFM results, however, it is difficult to determine the structures of both silicon films.

Fig. 2 and 3 show the bright field cross-sectional TEM images and selected area diffraction (SAD) patterns of the silicon films deposited without and with SiF_4 , respectively. Good sections with homogenous thickness were obtained with both silicon films. The thickness of the silicon film deposited without SiF_4 was found to be about 430 nm, and that with SiF_4 about 410 nm. The interfaces between the silicon films deposited without and with SiF_4 and substrates are flat, and no obvious changes in contrast were observed near or at the interfaces, indicating that the strains at the interfaces are small. The silicon film deposited without SiF_4 exhibits a featureless image (Fig. 2a), associated with a series of diffused halos in the SAD pattern (Fig. 2b), indicating an amorphous structure. A columnar structure growing in the direction perpendicular to the substrate was observed in the silicon film deposited with SiF_4 (Fig. 3a). The concentric circles of the SAD pattern shown in Fig. 3b indicates that the silicon film deposited with SiF_4 is polycrystalline.

Fig. 4 shows the dark field cross-sectional TEM images of the silicon film deposited with SiF_4 . The film was found to be made up of very small needle-like grains approximately 4 nm in width and 20 nm in length which are uniformly distributed in the thickness of the film. Tilting the specimen to 0°, 20° and 45° angles around the direction perpendicular to the substrate shows that the needle-like grains are perpendicular to the substrate.

Fig. 5 shows the XRD spectra of the silicon films deposited without and with SiF_4 . No peak from the silicon film deposited without SiF_4 was observed except the (111) peak of the silicon substrate (Fig. 5a). This indicates that the silicon film deposited without SiF_4 is amorphous, in good agreement with the TEM results. The spectrum shown in Fig. 5b contains the (220) peak of the silicon film as well as the (111) peak of the substrate. From the TEM and XRD results, it is suggested that there is a preferred orientation of the silicon film deposited with SiF_4 along the growth direction with the $\langle 110 \rangle$ of the film parallel to the $\langle 111 \rangle$ of the substrate.

Vatel et al. (5) studied the poly-Si growth during deposition on silicon using AFM, and suggested that the rugged mountains in an AFM image correspond to grains. From our results, however, the average diameter of the rugged mountains obtained from AFM does not coincide with the grain

size obtained from TEM, and the a-Si film shows the same morphological characteristic as the poly-Si film (Fig. 1). Therefore, it seems unreasonable to measure poly-Si grain size using AFM.

The structural difference between the silicon films deposited without and with SiF₄ can be explained by the etching effect of SiF₄. Without SiF₄, many dangling bonds and voids are located on the top of the SiO₂ film. The silicon atoms are immediately trapped right once they have arrived at the SiO₂ surface. Not enough time is available for silicon atoms to reach the position of thermal equilibrium. The subsequent silicon atoms easily adhere to the former ones trapped by voids and dangling bonds on the SiO₂ surface, so that amorphous silicon film subsequently forms⁽¹⁾. Another obstacle disturbing the growth of poly-Si films at low temperature is the impurities (especially oxygen and hydrogen) remaining in the vacuum chamber which cover and react immediately with the surface of growing silicon⁽²⁾. SiF₄ can etch out impurities such as oxygen and hydrogen bonds to form strong Si-F bonds (129 kcal/mol), and compensate for the voids on the SiO₂ surface⁽⁶⁾. The SiO₂ is more inert for silicon atoms to adhere in light of the dangling bonds and voids being compensated for, so silicon atoms have a longer time to reach the site suitable for crystalline phase network formation prior to being trapped. Therefore, with SiF₄, silicon atoms are more likely to form a crystalline phase.

4. CONCLUSIONS

The microstructure of the silicon films deposited without and with SiF₄ at low temperature by RPECVD was studied. Both silicon films have the same rugged surface morphology, but, the silicon film deposited with SiF₄ exhibits more rugged. The silicon film deposited without SiF₄ is amorphous, whereas the silicon film deposited with SiF₄ is polycrystalline with very small needle-like grains approximately 4 nm in width and 20 nm in length which are perpendicular to the substrate and uniformly distributed in the thickness of the film. The silicon film deposited with SiF₄ was found to have a preferred orientation along the growth direction with the <110> of the film parallel to the <111> of the substrate. The structural difference between the silicon films deposited without and with SiF₄ can be explained by the etching effect of SiF₄.

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REFERENCES

1. K.C. Wang, H.L. Hwang and T.R. Yew, Appl. Phys. Lett. 64 (1994) 1024.
2. T. Nagahara, K. Fujimoto, N. Kohno, Y. Kashiwagi and H. Kakinoki, Jpn. J. Appl. Phys. 31 (1992) 4555.
3. S.C. Kim, M.H. Jung and J. Jang, Appl. Phys. Lett. 58 (1991) 281.
4. Il-Jeong Lee, Shi-Woo Rhee and Sang Heup Moon, Appl. Phys. Lett. (submitted for publication)
5. O. Vatel, E. André, F. Chollet, P. Dumas and F. Salvan, J. Vac. Sci. Technol. B 12 (1994) 2037.
6. T. Wadayama, H. Kayama, A. Hatta and J. Hanna, Jpn. J. Appl. Phys., 29 (1990) 1884.

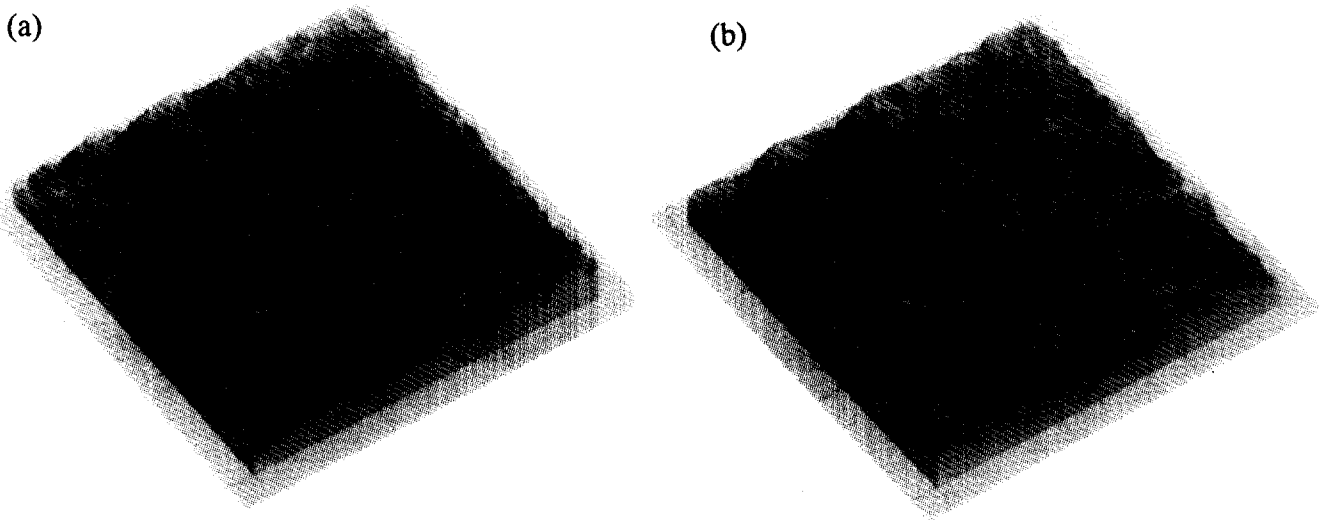


Fig. 1 Three dimensional AFM images of the silicon films deposited without (a) and with SiF_4 (b).

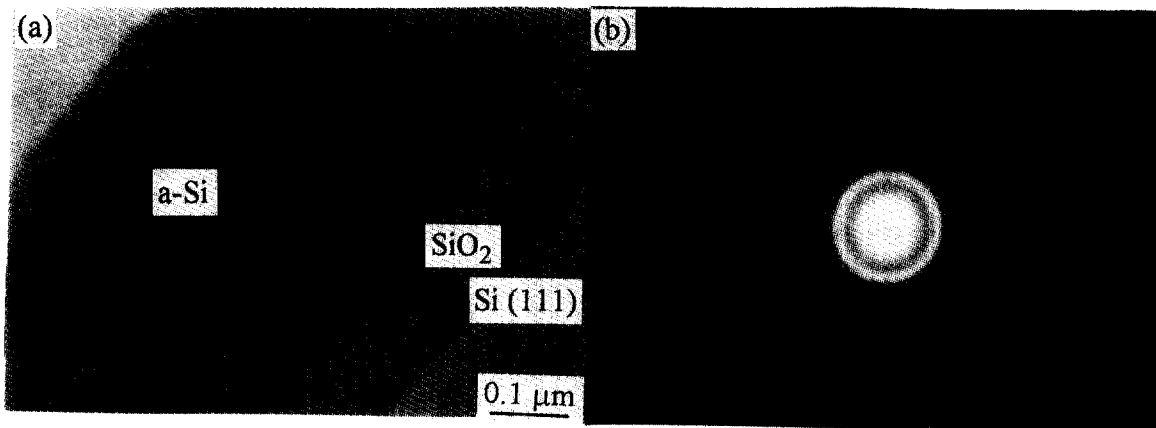


Fig. 2 Bright field cross-sectional TEM image (a) and SAD pattern (b) of the silicon film deposited without SiF_4 .

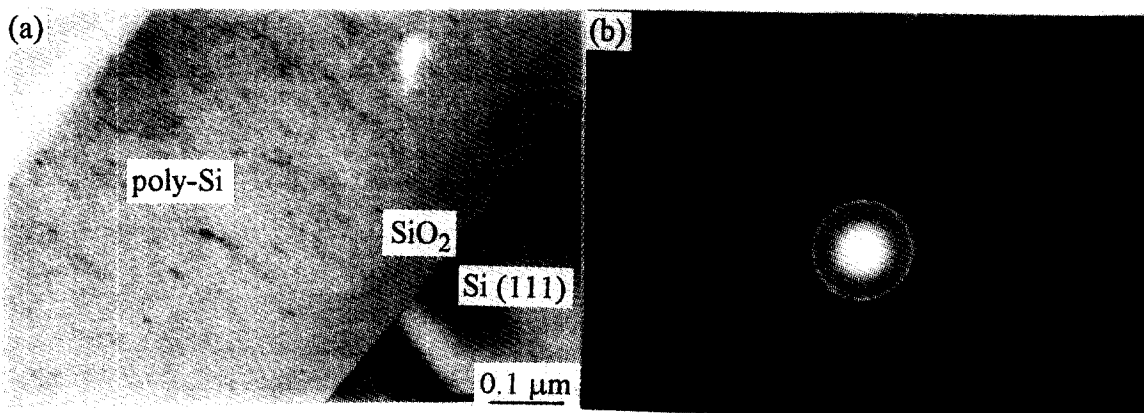


Fig. 3 Bright field cross-sectional TEM image (a) and SAD pattern (b) of the silicon film deposited with SiF_4 .

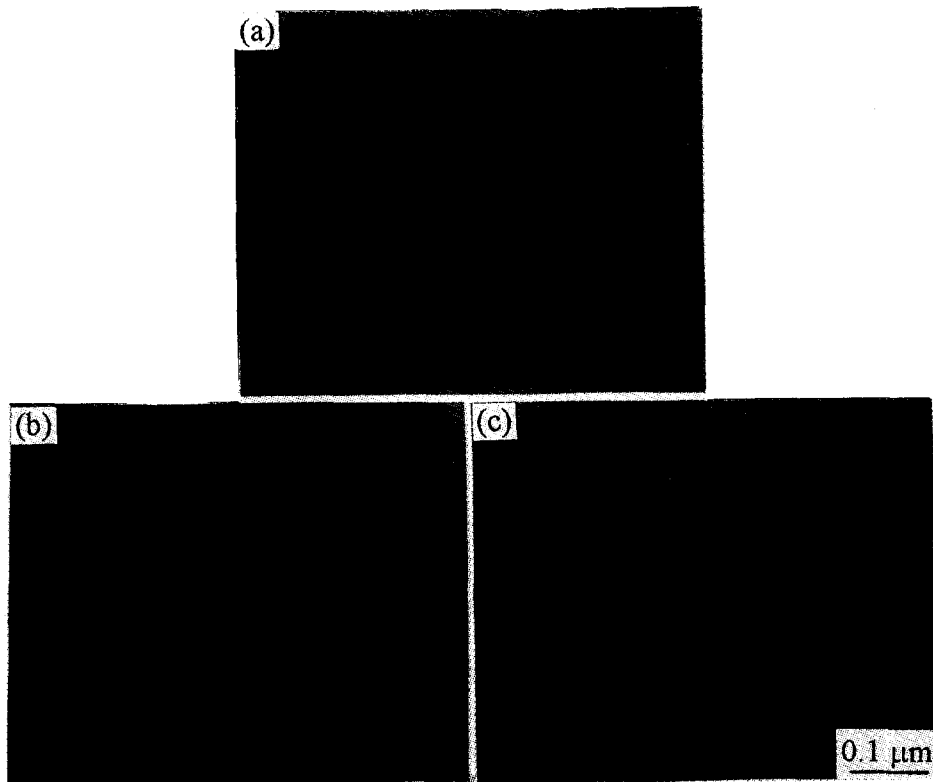


Fig. 4 Dark field cross-sectional TEM images of the silicon film deposited with SiF_4 obtained by tilting the specimen to different angles around the direction perpendicular to the substrate. (a) 0° , (b) 20° , (c) 45° .

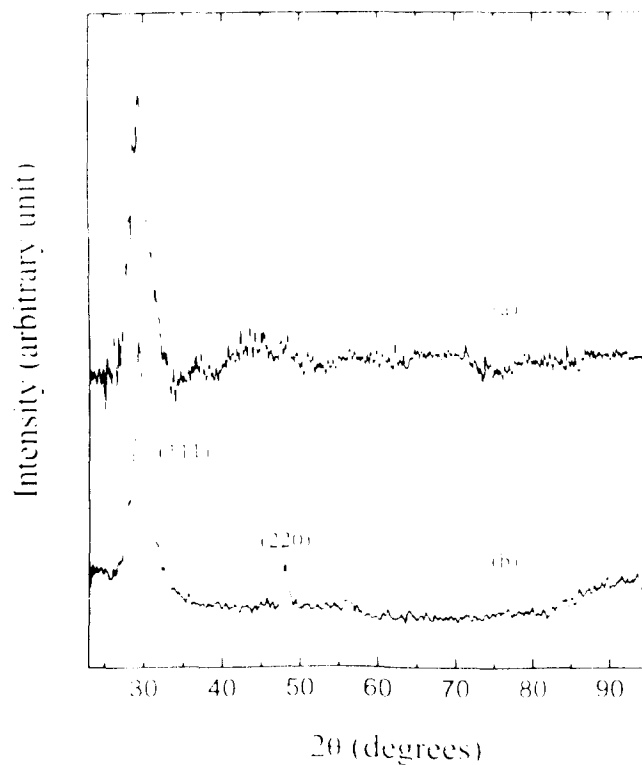


Fig. 5 XRD spectra of the silicon films deposited without (a) and with SiF_4 (b).