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INVESTIGATION ON THE COMPOSITION AND STRUCTURE OF SILICON NITRIDE FILM PREPARED BY ECR-PECVD

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In this paper, the effect of temperature on the composition and structure of the Si_3N_4 thin film is investigated. X-ray diffraction pattern and transmission electron microscope (TEM) analyses show that the Si_3N_4 film undergoes the transition from amorphous to crystalline phase with increasing deposition temperature. Infra-red qualitative analysis shows that the content of hydrogen decreases with increasing deposition temperature.The stoichiometric of Si_3N_4 is investigated by X-ray photoelectron spectroscopy or electron spectroscopy for chemical analysis.

PACC: 6855; 8115H; 5270

I. INTRODUCTION

The electron cyclotron resonance microwave plasma enhanced chemical vapour deposition (ECR-PECVD) is a high technology which has been developed since the 1970s. Owing to the high ionizability and density of the ECR microwave plasma (plasma density 10^{11}–10^{13} cm^{-3}),its activity is higher than that of DC and RF plasma for the PECVD. By using this character of ECR plasma, various high-quality, dense thin films can be deposited at room temperature.[1,2] Therefore ECR microwave plasma technology has become an important processing method in high technology fields,such as materials science, microelectronics, optoelectronics,[3] etc.

The Si_3N_4 thin film is a kind of hard ceramic film and has fine mechanical, optical and electrical properties. The Si_3N_4 films prepared by the chemical vapour deposition (CVD), the laser plasma chemical vapour deposition (LPCVD), the radio-frequency enhanced plasma chemical vapour deposition (RF-PECVD) methods have practical application. But in many fields, there is a great need of dense texture Si_3N_4 film deposited at lower substrate temperature. The technologies indicated above cannot meet the requirement. Si_3N_4 film prepared by the ECR–PECVD method has the advantages of lower substrate temperature, high step cover,fine insulation, good uniformity, good corrosion resistance and stable performance etc.[4,5] As a result, it has been applied to the fabrication of semiconductor and optical devices[6] (phase-change optical disks, solar energy cell), the final passivation of integrated circuits, and the intermediate medium of multi-layer metallic structure as well.

In this paper, the Si_3N_4 thin films were prepared by ECR–PECVD method at the deposition temperature ranging from 40 to 460°C. The composition and structure of the film have been evaluated by infra-red (IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS) or electron spectroscopy for chemical analysis (ESCA).

II. PREPARATION OF Si_3N_4 FILM

Figure 1 shows schematically the ECR-PECVD apparatus for deposition of Si_3N_4 designed by ourselves. The apparatus consists of a vacuum pumping, a gas puffing, a microwave excitation, a reaction chamber and a substrate subsystems. The vacuum pumping subsystem is composed of a turbomolecular pump and a mechanical pump, the gas puffing subsystem,a SiH_4 and a N_2 gas sources, and a mass flow meter with double paths as well. The microwave excitation subsystem includes a microwave source, whose power can be continuously adjusted up to 600 W, and a microwave input matching coupler. The reaction chamber subsystem is composed of two coils with a DC power supply, and a stainless-steel tube (ϕ14.5 cm×100 cm) with a microwave window. The substrate subsystem is a substrate frame whose axial position can be adjusted, and the substrate can be heated from room temperature to 460 °C by adjusting the substrate heating power supply.

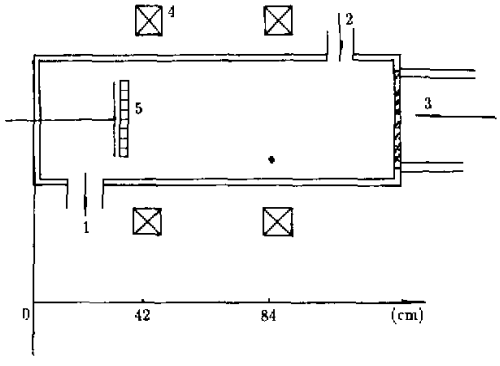


Fig. 1. ECR-PCVD apparatus. 1: Vacuum pumping subsystem; 2: Gas puffing subsystem; 3: Microwave excitation subsystem; 4: Coils; 5: Reaction chamber and substrate.

The background vacuum degree is higher than 2×10^{-3} Pa, and the operation pressure 8×10^{-2} Pa. Because of the effect of magnetic confinement and the electrons heated in the resonant area, the high-density plasma is produced within a quite long axial region. Figure 2 shows the axial profile of the magnetic field and plasma density, which in the resonant area is about 1.8×10^{11} cm^{-3}. The Si_3N_4 film is made on the Si or KBr wafers put on the substrate frame.

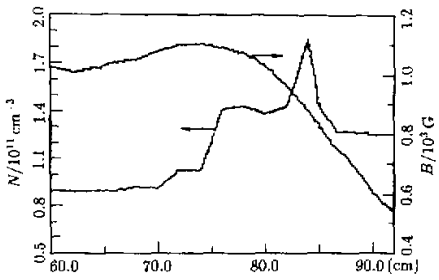


Fig. 2. The axial profile of the magnetic field and plasma density.

III. RESULTS AND DISCUSSION

A. IR spectra analysis

The IR spectra of Si_3N_4 film are tested with a NICOLET170SXFIR instrument (wave number accuracy is $0.01\,cm^{-1}$, resolution ratio $4\,cm^{-1}$, scanning frequency 60). Figure 3 shows the dependence of the IR transmission spectra of samples 1,2,3,4 and 5 on the corresponding deposition temperatures of 40 °C, 200 °C, 280 °C, 360 °C, 460 °C respectively. In IR spectrograms of samples 1 and 2, N–H bond peaks appear around the wave number $3360\,cm^{-1}$, which results from N–H stretching mode[7], while Si–H bond peaks lie around $2160\,cm^{-1}$, which is caused by Si–H stretching mode. The N–H and Si–H bond peaks of sample 1 are bigger than that of sample 2, meaning that sample 1 contains more H than sample 2. In IR spectrograms of samples 1 and 2, N–H bond peaks are located near $1200\,cm^{-1}$, which are produced by N–H bending mode, while Si–N bond peak, which results from the Si–N stretching mode, is around the $870\,cm^{-1}$. Compared with other peaks, the last is the highest. Around $500\,cm^{-1}$, there is a peak of Si–N generated by bending mode. In the spectrograms of samples 3,4 and 5, the highest Si–N stretching-mode peak around $870\,cm^{-1}$, and the Si–N bending-mode peak around $500\,cm^{-1}$ are shown, while Si–H and N–H peaks are not. That means, the content of hydrogen in Si_3N_4 film decreases with increasing deposition temperature.

The H content in Si_3N_4 film decreases with increasing deposition temperature, because the Si and N atoms in the reactor combine easily with each other forming Si–N bond to produce Si_3N_4 film, and the H atoms are easier to combine together, producing H_2 molecules, which can be exhausted as a waste gas. The H_2 gas which permeates into the film can be released from the depositing film surface when the substrate temperature is high enough. The N–H bond is less stable than the solid phase Si–N bond. When substrate heated, the N–H bond will be resolved and released from the film of Si_3N_4. The high content of H in the

Si_3N_4 film can affect corrosion resistance of the Si_3N_4 film, the threshold voltage in VLSI device application, and other properties.[8] So the decreasing of H content can improve the Si_3N_4 film properties. This result points out that by ECR-PECVD method the Si_3N_4 film can be prepared with low enough content of H when depositing temperature is 280°C. In Refs.[7,9,10], it was reported that the H content in the Si_3N_4 film prepared by ECR-PECVD was lower than that prepared by RF-PECVD.

Figure 3 shows that the transmissive peak at around 830 cm^{-1} has a slight shift towards higher frequency with increasing deposition temperature, The films having higher frequency transmissive peak are denser.[11] The shift of the peak for sample 3 is small, and that for sample 4 or 5 large. Figure 3 also displays that IR transmissivity decreases with increasing deposition temperature, showing that the density can be improved with increasing deposition temperature.

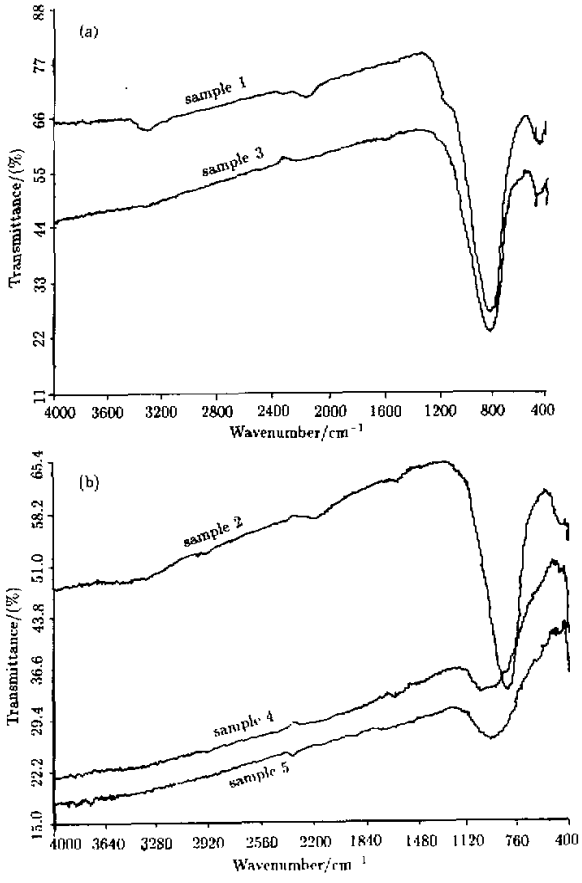


Fig. 3. IR spectra of Si_3N_4 film.

B. XRD and TEM analyses

The samples 1 and 3 are also investigated by XRD and TEM. The XRD patterns are shown in Fig.4(a), (b). The X-ray diffraction pattern of sample 1 indicates that the film is amorphous. In XRD pattern of sample 3, there is a small diffraction peak at diffraction angle 26.5 °. The sample 3 may exist in partial crystalline structure.

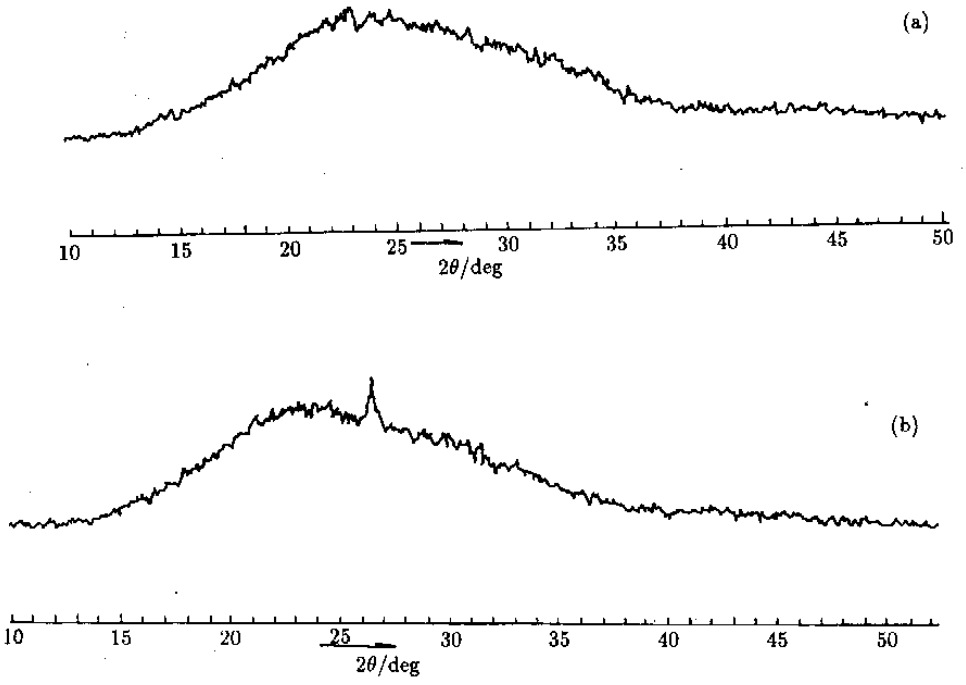


Fig. 4. XRD patterns.

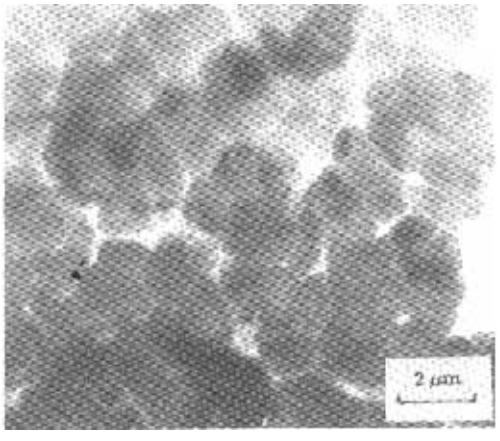
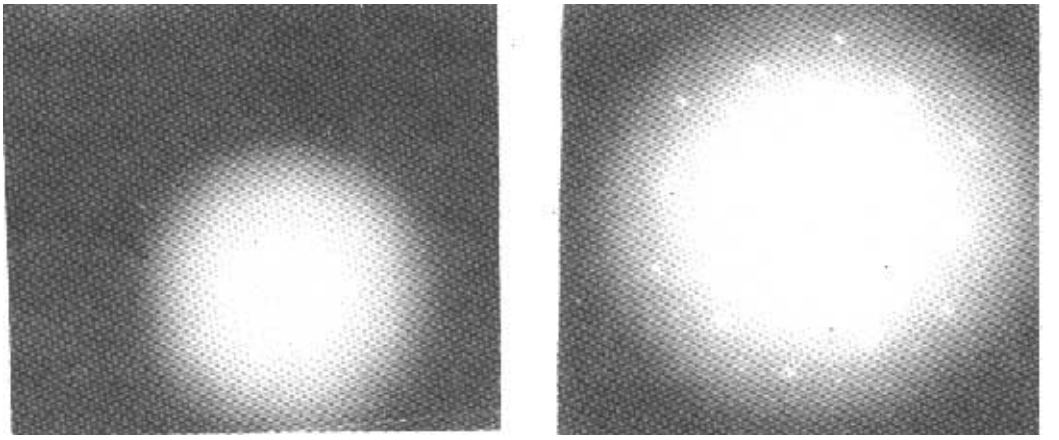


Fig. 5. TEM picture.

Figure 5 shows the TEM picture of sample 1, which shows that the Si_3N_4 film surface is composed of many uniform large islands, most of the boundary between neighboring islands join each other, a small part of the joining area has only very small gap. This result indicates that the surface of Si_3N_4 film is uniform and the structure densely packed without pin holes. Figure 6 shows the electron diffraction patterns for samples 1 and 3. The pattern for sample 1 appears to be dispersion halo, indicating that sample 1 is an amorphous Si_3N_4 film. On the dispersion halo of the electron diffraction pattern for sample 3 appear electron diffraction spots with hexagonal symmetry, which are produced by electron beam incident along the axis of hexagonal symmetry, i.e., there is crystallization in the film. The crystal belongs to a hexagonal system[12], and the Si_3N_4 crystalline state is of hexagonal

system[5], so the film is determined to be crystalline Si_3N_4 film. The results above show that the crystalline Si_3N_4 film can be prepared by ECR–PECVD method at suitable deposition temperature. Reference [13] reported that Si_3N_4 film prepared by DC–PECVD method was amorphous, which can transform from amorphous to crystalline state after annealing at 1050°C. But in this work crystalline Si_3N_4 can be formed around 280°C by utilizing ECR–PECVD method.



(a) Sample 1 (b) Sample 3

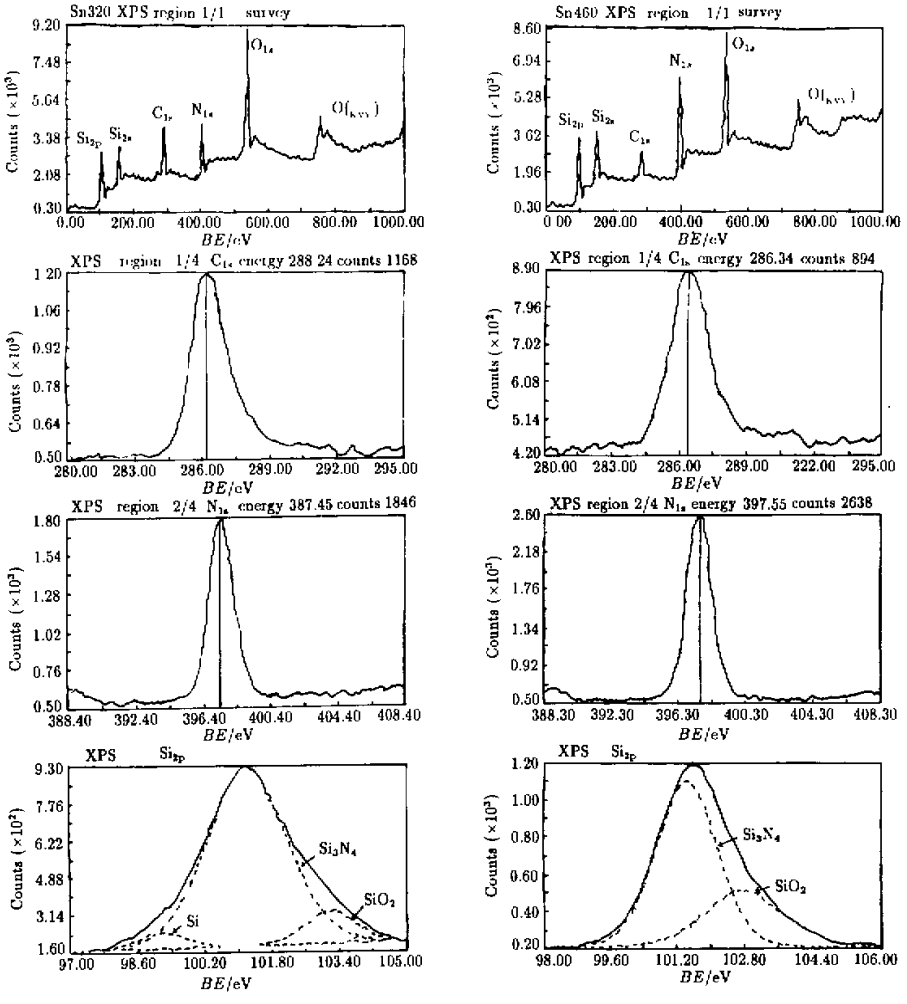
Fig. 6. TEM electron diffraction patterns.

C.XPS analysis

The X-ray photoemission spectra for samples 2 and 5 shown in Fig.7 were tested and analyzed with an Y.G. ESCA-LAB-MK-II energy spectrum instrument. There are Si_{2p}, Si_{2s}, C_{1s}, N_{1s}, O_{1s}, $O_{(KVV)}$ peaks in the whole spectra of XPS, where the C_{1s} resolved spectrum is used for calibrating the spectrum. From the Si resolved spectrum of sample 2, it can be seen that the singlets Si, Si_{2p} and SiO_2 are contained in Si energy spectrum. However, from the Si resolved spectrum of sample 5, the singlet Si is not contained in it and there exist only Si_{2p} and SiO_2. The Si_{2p} is an element factor forming Si_3N_4. The calculation results evince that the stoichiometric relations for samples 2 and 5 are 1.60705 and 0.92, respectively, and that the stoichiometric relation for sample 5 is close to 0.75.

From the analyses mentioned above, in the Si_3N_4 film the singlet Si which does not participate in the reaction is decreased and the stoichiometric relation becomes close to 0.75 with increasing deposition temperature. The chemical reaction between Si and N is enhanced with increasing deposition temperature and that the formation of Si_3N_4 product is facilitated. But there is a part of SiO_2 in the Si_3N_4 film in sample 5, which is probably

produced via a reaction between Si and O_2 that may remain in the vacuum chamber and can be decreased by raising the background vacuum.



(a) Sample 2 (b) Sample 5

Fig. 7. XPS energy spectra.

IV. CONCLUSION

The fine Si_3N_4 thin film has been prepared by ECR-PECVD method at deposition temperatures ranging from 40 to 460 °C.

XRD and TEM analyses show that the crystalline Si_3N_4 thin film can be prepared at a suitable deposition temperature.

IR analysis shows the H content in the Si_3N_4 film decreases with increasing deposition temperature, which will improve the electrical and chemical properties of the Si_3N_4 thin film.

XPS analysis shows that the stoichiometric relation of Si_3N_4 film is close to 0.75 with the increase of deposition temperature and the background vacuum degree.

In summary, high quality Si_3N_4 film can be prepared by ECR-PECVD method through controlling deposition temperature, and this kind of Si_3N_4 film may satisfy some special requirements.

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