Transactions of the Materials Research Society of Japan. Vol. 20

Studies of α-SiC thin film prepared by pulsed XeCl excimer laser

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Nearly stoichiometric α-SiC films were deposited on [100] and [111] Si wafers by laser ablation of ceramic SiC targets. Before and after annealing, the structure, morphology and composition of the sputtered films were studied by AES, XPS, XRD, IR and PL. We found that the unannealed α-SiC films were polycrystal and after annealing they turned into monocrystal 4H-SiC. Further fluorescence analysis confirmed the result of XRD, that the band structure of the annealed SiC film is of 4H type. Excited by 290nm laser, the films show two emission peaks at 377nm and 560nm. The peak at 377nm can be due to interband recombination. There are three possible mechanisms given to express the emission at 560nm.

1. Introduction

Due to the wide band gap, high chemical stability and other unique properties[1], there are more and more interests in the studies of SiC. The SiC films have shown important and potential applications in many fields such as electronics, photoelectronics and so on. Therefore, preparation of SiC films and analysis of its properties becomes an important subject in these fields. Recently SiC thin films were mostly grown by chemical vapor deposition(CVD)[2]. It is not familiar to prepare the SiC films using pulsed excimer laser deposition(PLD)[3]. In this paper we systematically study the quality and the structures of the SiC films deposited by PLD and give some useful results.

2. Experiment details

The experimental apparatus is similar to the one used in previous studies of laser ablation of high temperature superconductor materials[4]. The tilted XeCl excimer laser with wavelength 308nm, energy 190mJ, pulse width 25ns and laser repetition rate 10 Hz was focused to a spot size of 2 × 3mm^2 on a SiC ceramic target through a quartz window. The power density was 2~4J/cm^2. The films were deposited with base pressure 5 × 10^{-5} Torr. During deposition, laser scan and target scan procedures were conducted to uniform the composition and the thickness of the films. The substrate was single crystal Si(100) paralleled to the target. It was located 6cm from the target, heated in a resistance heater tube with a temperature range from 30 ℃ to 900 ℃ and within the accuracy of 50 ℃. The substrate was pre-treated as usual in substrate washing and heated to 850 ℃ for 30 minutes to remove the native oxide. Deposition of the films was kept for 30 minutes on Si(100) at 850 ℃.

We studied the composition, chemical states and structure of the films, using SEM, XRD, AES, XPS, IR and PL.

3. Experimental results and discussion

3.1 XRD analysis

X-ray diffraction patterns of the thin films were taken by a D/max-rA rotating target X-ray diffractometer, with Cu K_α radiation. Figure 1(a) and 1(b) show X-ray diffraction spectra of SiC films deposited on Si(100) at substrate temperature of 850 ℃ and the ones deposited under the same conditions annealed for an hour at 1000 ℃ in vacuum (3 × 10^{-5}Torr), respectively. Comparing the d values listed in Fig.1(a) with the ones in literature[5], we found that our films were polycrystal 4H-SiC films. There is only one peak observed at d value of 2.698Å in the XRD patterns of the annealed films (Fig. 1(b)), while there are four before annealing. The peak at d value of 2.698Å corresponds to the diffraction of (100) plane of 4H-SiC crystal. This result indicates that after annealing the films turn to singlecrystal epitaxial films along the [100] orientation.

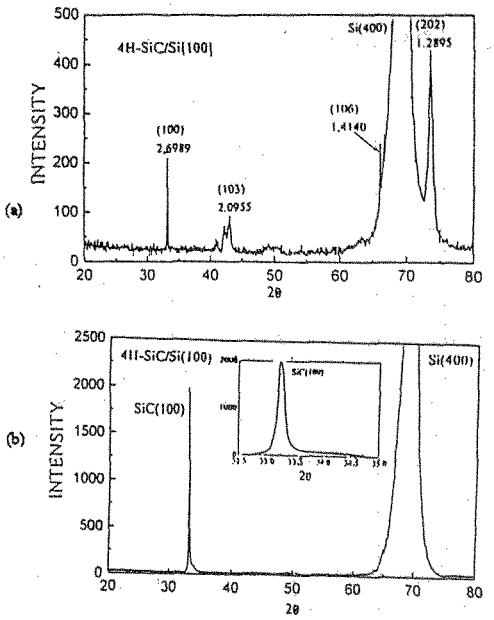


Figure 1 XRD patterns of the films (a) before (b) after annealing

3.2 SEM analysis

From cross-sectional SEM micrographs of the films, we find that the films stick tightly to the substrates. The thickness of the films measured by the surface analysis system is 12μm and the deposition rate is 0.6nm per pulse.

Fig. 2 shows the SEM image of SiC/Si(100) films. It indicates that the surfaces of the films are dense, uniform and relatively smooth and contain a few inclusions. The similar inclusions were observed in the previous studies of laser ablation of high temperature superconductor materials.[6]

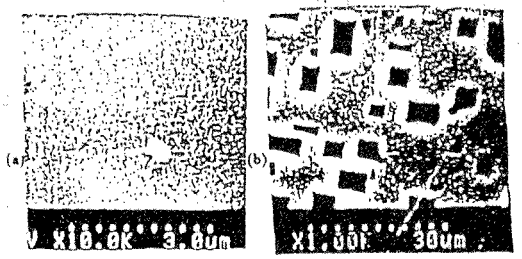


Fig.2: SEM image of the films (a) before (b) after annealing

There are three possible explanations to express the formation of the inclusions, given in ref.[6]. It can be seen from Fig. 2(b) that after annealing there are a large amount of square patterns formed near the surface. Therefore, there was a recrystallization procedure of crystal orientation ordering during annealing. This process was constrained by the orientation of the substrates. The constraint mechanism is to perform the best match of crystal lattice and the lowest binding energy. This process resulted in the formation of epitaxial films. It is thus concluded that during annealing the structure of the films turned from polycrystals to epitaxial crystal films along [100] orientation with forming a large amount of dislocations.

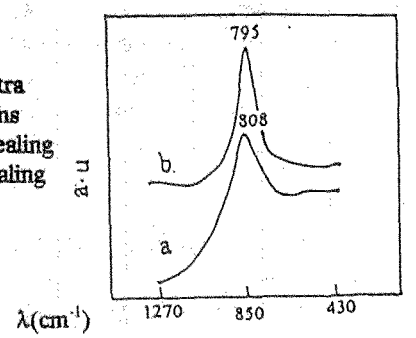


Fig. 3: IR spectra
of the films
(a) before annealing
(b) after annealing

3.3 IR analysis

Fig. 3(a) and Fig. 3(b) show the IR absorption spectra of SiC films before and after annealing, respectively. Before annealing there is a peak at 808 cm^{-1} with FWHM (full-width-at-half-maximum) about 72 cm^{-1}, and after annealing around 795cm^{-1} with FWHM approximately 32 cm^{-1}. According to literature[7], the peak due to the absorption of the characteristic Si-C bond in the TO stretching mode in singlecrystal SiC is at 795 cm^{-1} with FWHM 27cm^{-1}. Therefore, before annealing the films were already formed of Si-C covalent bonds although the integrity of the bonds was not perfect. Furthermore, after annealing, the peak shifted to 795cm^{-1}, FWHM changed to 32 cm^{-1}. So the position of the peak is the same as that in singlecrystal SiC and FWHM is a little different. This result suggests that the films are almost changed to singlecrystal structure after annealing and the integrity of the structure also improved. In summarize, our films consist of Si-C covalent bonds, annealing can improve the integrity of the structure and the films almost turned into singlecrystal SiC ones.

Table 1: Photoelectron peak's energy, width and chemical shift (ev)

Sample name	Si(2P)	Δ_{Si}	C(1s)	Δ_C	O(1s)	Δ_O	O(1s) Chemical shift	C(1s)-Si(2p)	Chemical shift
Si	99.6	1.5							
Graphite			284.5	1.5				184.9	0
SiC monocrystal	100.6	1.7	282.9	1.7	531.7		0	182.3	2.6
1#SiC/Si (100)-850°C	100.45	1.9	283.6	2.0	531.7	2.1	1	183.15	1.75
1# annealed at 1000°C	101.2	1.9	283.7	2.33	532.3	2.0	1.6	182.5	2.2

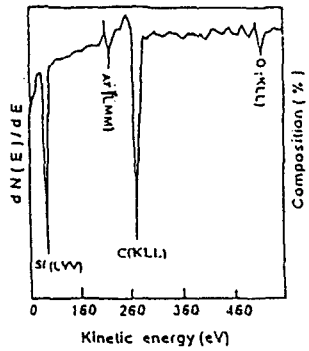


Fig.4: AES of the films

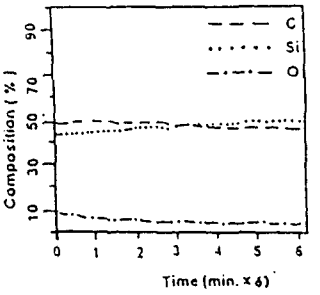


Fig.5: AES depth profile

3.4 AES analysis

AES and XPS of thin SiC films were performed using an ESCALAB MK-II system, combined with an Ar^+ ion gun(1.5kev, 20μA, 5min) for sputter etching. Fig.4 shows the AES spectrum of the SiC films. It can be found in Fig.4 that the main elements of the films are silicon and carbon and the films contain a little oxide contamination. From the intensity of the Si(2p) and C(1s) peaks we estimated the ratio of silicon to carbon nearly 1:1(a slightly more carbon).The inner of the films contains of oxide contamination about 5 percent.

The Auger depth profile for the films is given in Fig.5. The composition of the films is almost constant over its entire thickness and the ratio of silicon to carbon calculated is also nearly 1:1. The surface layers of the films contain of oxide about 10 percent and the inner 5 percent noise level.

3.5 XPS analysis

Fig.6 shows the XPS of the films. There are some XPS data of the films under different preparation conditions, O_2, graphite and monocrystal SiC, listed in table 1. The FWHM of Si(2p), C(1s) and O(1s) in table 1 are expressed as Δ_{Si}, Δ_C and Δ_O ,respectively. The interval of the two peaks is indicated as C(1s)-Si(2p).

It can be seen from Fig.1 that before annealing the chemical shift of the SiC films is about 1.75ev and FWHM 1.9~2.3ev, and after annealing they change to around 2.2ev and 1.9~2.3ev, respectively. This implies that the chemical shift increases and FWHM does not change with annealing.

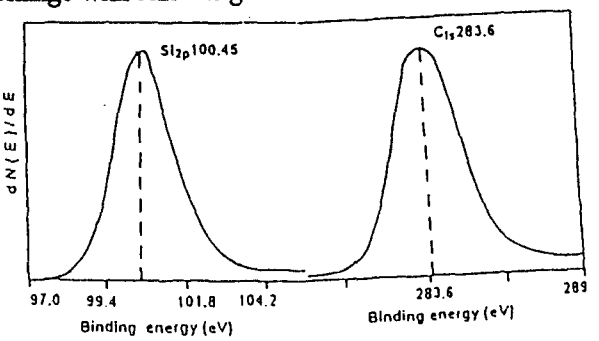


Fig.6: XPS of the films

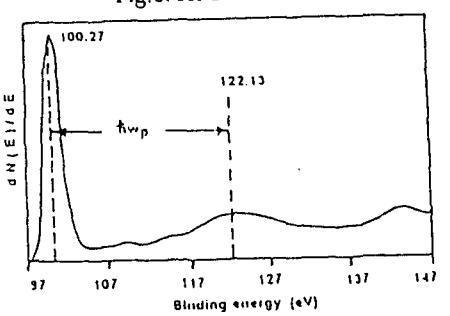


Fig.7: Energy loss spectrum

Table 2: Values of direct optical gaps in 4H-SiC measured in this work and in ref. [9]

Excitation spectra	wavenumber(nm)	250	292~290	532	548	580
Excitation spectra	energy(ev)	4.96	4.56~ 4.58	2.33	2.26	2.13
Electronreflection[9]	energy(ev)	4.98	4.58	2.60	2.17	2.10
Theoretical calculation[9]	energy(ev)	4.97	4.65	2.75	2.20	

Fig.7 is the Si(2p) energy loss spectrum of the samples. From Fig.7, the energy of polariton $\hbar w_p$ is around 21.86ev while that of monocrystal SiC is 22.5ev, and those of Si and C are 17ev and 17.5ev, respectively. Therefore, the basic structure of SiC films deposited by PLD consists of Si-C covalent bonds. At the same time, according to

$$\hbar w_p=(4\pi h^2 n_e e^2/m_e)^{1/2} \quad \text{ref.[8]}$$

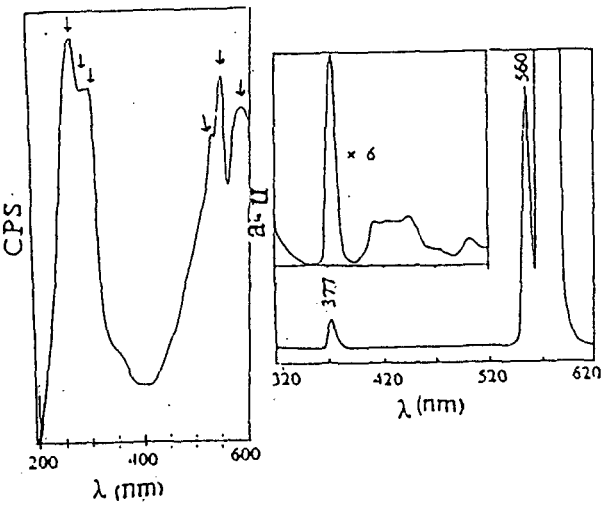
we calculate the ratio of the density of the valence electron n_e in the films to that in the monocrystal SiC (i.e. $(21.6/22.5)^2$=94.4%). On the other hand, we know from ref.[6] that the electron density of the ideal amorphous SiC is only 91-93% of that of monocrystal SiC even with all the bonds saturated.

3.6 PL analysis

The excitation spectra and photoluminescence of the annealed films were performed at room temperature on 850-type fluorescence spectra-photometer. Fig. 8(b) is photoluminescence (PL) spectra of the films exited by 290nm laser. V.I.Gavrilenko[9] et al. have studied the band structure of SiC thoroughly. The direct band gap of 4H-SiC measured by ER spectra and theoretically calculated and our values obtained from excitation spectra are listed in table 2.

From table 2 we know that our values obtained from excitation spectra are identical to that given in ref. [9] except the one at 2.33ev. This indicates that the band structure of our SiC films is similar to the direct-transition band structure of 4H-SiC in ref. [9]. The values measured by excitation spectra correspond to the direct band gap, too. Therefore, it is concluded that the films are of crystal 4H-SiC structure. This confirmed the result of XRD analysis.

There are two emission peaks in Fig. 8(b). One is at 377nm and the other 560nm, corresponding to energy 3.28ev and 2.21ev, respectively. From ref. [9], the forbidden band gap of 4H-SiC is 3.28ev. Therefore, the emission at 377nm is due to the interband recombination of electrons and holes. As for the one at 560nm, there are three possible mechanisms: First, it is assigned to the emission of recombination of Al acceptor centers or Al-O donor-acceptor pairs, since Al contamination is observed in X-ray fluorescence analysis (atomic density is about 8×10^{-5}). Al contamination could come from the ceramic SiC target. The second explanation to the 560nm emission is the complex emission mode formed by dislocations in the films. The third is the direct subband transition at M point in the Brillion Zone.



(a) (b)

Fig.8: (a) excition spectra (b) PL

Conclusions

The main results of this paper are summarized as follows:

1. We successfully prepare SiC films with a dense and uniform structure stuck tightly to the substrates using pulsed excimer laser deposition method. The deposition rate is about 0.6nm per pulse.
2. Increasing substrate temperature and anneal-

ing both improve Si-C bonding and crystal quality of the films.

3. The composition of the films is uniform over its entire thickness. The ratio of silicon to carbon is nearly 1:1, except for a little oxide. The basic valence in the films is Si-C covalent bond. The density of valence electron is 94.4 percent of that of single crystal SiC.

4. The annealed films are of 4H-SiC crystal structure. There are some epitaxial dislocations in the films.

5. The direct band gaps measured by excitation spectra agree with that taken by ER in ref. [9].

6. Excited by 290nm ultraviolet laser, the films emit two bands at 377nm and 560nm. In our view, the emission at 377nm is due to interband recombination of electrons and holes. As for the one at 560nm, possible explanations are: recombination of the Al contamination acceptor centers, Al-O donor-acceptor pairs, or direct subband transitions at M point in the BZ.

The results of structural analysis were obtained in the Structure Research Laboratory USTC. Here, give thanks to Guien Zhou, Yunbo Jia, Jianxin Wu, Kelian Hu, Zitai Song, Jian Lu, Li Yan et al. Also give thanks to Dehui din of Institute of National Building Materials for SiC bulk sources. This project is financially supported by National Fundamental Committee of China.

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