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Dependency of reactive magnetron-sputtered SiC film quality on the deposition parameters

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Abstract

SiC thin films have been prepared by using RF reactive magnetron sputtering (RF-RMS). The deposition parameters have been varied over a wide range to optimize the quality of the films; substrate temperature from 700 to 1000°C, Ar/CH_4 composition from 80:20 to 50:50 and RF power from 100 to 200 W. The samples have been characterized by X-ray diffraction, Rutherford backscattering, profilometry, FTIR spectroscopy and ellipsometry. The results show that good quality silicon carbide films can be prepared by using the RF-RMS technique. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon carbide; RF reactive magnetron sputtering

1. Introduction

Amorphous silicon carbide (a-$Si_{1-x}C_x$) is an attractive material from a technological point of view. Its electronic and optical properties make it potentially useful as a solar selective coating. In addition, because of its high temperature resistance, wide band gap and high electron saturation velocity, a-$Si_{1-x}C_x$ alloy is a good candidate for stable high-T semiconductor and high power devices [1].

This material has been prepared by various techniques such as chemical vapor deposition (CVD) [2], plasma-enhanced chemical vapor deposition (PE-CVD) [3], reactive magnetron sputtering (RMS) [4], etc. In recent years, an extensive experimental effort has been devoted to the study of a-SiC [5]. However, a complete understanding of the relation between its physical properties and the preparation process is still lacking.

We started work on the preparation of crystalline SiC thin films using the RMS technique after the work of Wahab et al. [6,7] who reported, for the first time, the preparation of cubic SiC thin films using this technique. We used the same technique and the same preparation conditions as they used but our results are very different. We have obtained amorphous films and have studied the dependency of reactive sputtered films on the deposition parameters. The parameters such as temperature and the ratio of argon to methane have been changed over a wide range and a correlation of the deposition parameters with the physical properties of the SiC films is proposed.

2. Experiment

The films were grown in a turbomolecular-pumped ultrahigh vacuum sputtering system with a base pressure of 3×10^{-7} torr. The RMS technique was used in a mixed Ar/hydrocarbon plasma. The system was equipped with a 4-inch magnetron source and the target material was a high purity (99.999%) electronic grade silicon disc which was clamped against the water-cooled cathode surface. Sputtering was carried out in mixed Ar-CH_4 discharges at different powers of

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RF. The purity of Ar and CH_4 gases was 99.999%. For this work, the pressure, total gas flow and target to substrate distance were kept constant at 3 mtorr, 10 sccm and 3 cm, respectively. The substrates were pieces of Si(100) wafers which were chemically cleaned prior to the insertion in the vacuum chamber. The substrates were cleaned in $NH_4OH:H_2O_2:H_2O$ and $HCl:H_2O_2:H_2O$ for 5 min each, then rinsed with ionized water. The deposition parameters were varied over the following range:

- RF power: 100 and 200 W
- Gas composition: 80:20, 70:30, 40:60 and 50:50 Ar/CH_4 ratio for each value of RF power
- Substrate temperature, $T_s = 700–1000°C$ for each set of gas compositions.

When the substrate temperature was at the required value, CH_4 was introduced to a pressure P_{CH4} of 0.6 mtorr for 10 min to carbonize the surface of the silicon. Then the P_{Ar} was increased to obtain $P_{tot} = 3.0$ mtorr, the pressure maintained throughout the deposition. The discharge was then ignited. The Si target was sputter-cleaned for 5–10 min. The shutter between the target and substrate prevented deposition of sputtered material on the latter. Subsequently, the shutter was removed and growth initiated at a constant discharge power. Graphite and, in some cases, a 1-mm wide strip of silicon, was used to mask the edge of the silicon substrate and in this way a step was formed between the edge of the deposit and the substrate. This step was used to measure the film thickness by a profilometer.

All the samples have been studied by X-ray diffraction using a Siemens Diffractometer, model D500, of the Institute of Materials Science, IIM. The ion beam analysis (IBA) facilities at the University of Mexico [8] based on a vertical single ended 5.5-MeV Van de Graaf accelerator (in the Institute of Physics) films and its associated instrumentation were used to obtain the areola density and the elemental composition of SiC films. The produced spectra were analyzed using the RUMP software package [9] developed by Cornell University. The thickness of the films was found using the Gaertner ellipsometer (model L117) and a Dektak IIA perfilometer. For the evaluation of refractive index, the same ellipsometer was used.

For the analysis of plasma, an optical emission spectroscopy OES was employed. The monochromator was an Oriel model 77250 machine with a 1200 lines/mm grating usable from 300 to 950 nm. The optical detector was an Hamamatsu model R955 side window photomultiplier used in conjunction with a Hamamatsu preamplifier. For optical measurements, a Nicolet model 205 FTIR was employed with a measurement range of 400–4000 cm^{-1}.

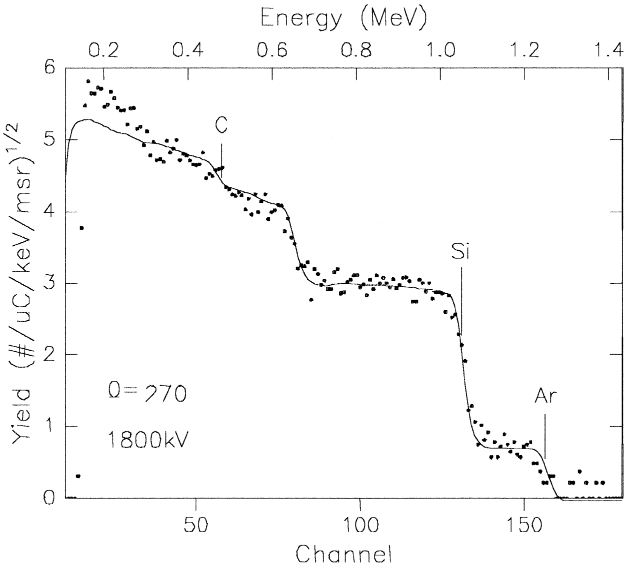

Fig. 1. A typical RBS spectra from a SiC sample.

3. Results

According to the X-ray diffraction data, there is no prominent peak indicating the formation of crystalline SiC films.

A typical spectra from RBS is shown in the Fig. 1. This was used to calculate the silicon to carbon ratio, R, and also used to detect the impurities in the films. In some of the deposits, approximately 1% of Fe and oxygen were found. The areal density (gm/cm^2) and the elemental composition of the SiC films were obtained from the simulation of the elastic region of the spectra. An empirical estimation of the error in the areal density and the composition of the films is approximately ±5%.

Fig. 2 shows the variation of R with substrate temperature T_s at 100 W of RF power. The curves A, B and C indicate R vs. T_s variation at a fixed composition 80:20, 70:30 and 60:40 of Ar/CH_4, respectively. Curve A shows that R remains, almost, constant with increasing temperature. The curves B and C show that R increases from the stoichiometric value with T_s smoothly. The R vs. T_s variation for 200 W of RF power is shown in Fig. 3 where the curves A and B represent this variation at a gas composition of $Ar/CH_4 = 80:20$ and 70:30, respectively. From these curves, it is observed that there is almost no change in R when temperature is increased.

The density ρ (gm/cm^3) has also been calculated by using the areal density and the thickness of the films. Fig. 4 shows the variation of ρ vs. T_s from 800 to 950°C at RF power of 100 W where the curves A, B and C represent this variation at fixed concentration of CH_4 = 20%, 40% and 50%, respectively. It is observed that there is an increasing trend in the variation of ρ for the

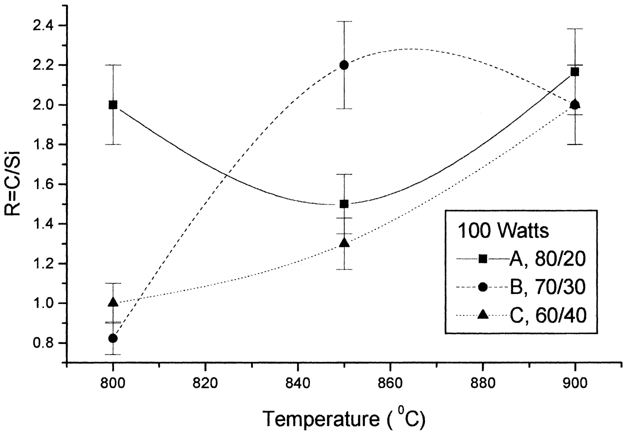

Fig. 2. The variation of the sample composition vs. the substrate temperature for a plasma power of 100 W. The curves A, B and C are for the gas mixtures Ar/CH_4 of 80:20, 70:30 and 50:50, respectively.

curve A while the curve B decreases with increasing T_s. However, there is no variation in ρ with temperature for the curve C. The ρ vs. T_s variation for RF power of 200 W is shown in the Fig. 5 where the curves A, B, C and D represent the density curves at fixed concentration of $CH_4 = 20\%$, 30%, 40% and 50%, respectively. The density curves A, C and D have an increasing trend of the variation of ρ with T_s while in curve B, ρ remains constant with temperature.

The deposition rate (DR) is also an important parameter in the preparation of SiC thin films which helps to explain the optical and structural properties of a-SiC films. According to the DR curves, it is observed that DR decreases with increasing T_s for 100 W of RF power, while for 200 W of RF power, DR increases with the increase of T_s. It has also been observed that the refractive index, n, has almost the same trend of variation with temperature for 100 W and 200 W of RF power i.e. n decreases with the increase of T_s. Fig. 6 shows the variation of n with Ar/CH_4 composition at fixed value of the substrate temperature where the curves P_1 and P_2 represent the variation for 200 W and 100 W of RF power, respectively. According to this, it is observed that both curves demonstrate an opposite trend of variation of n with the concentration of CH_4 which means that n decreases for 100 W while it increases for 200 W of RF power.

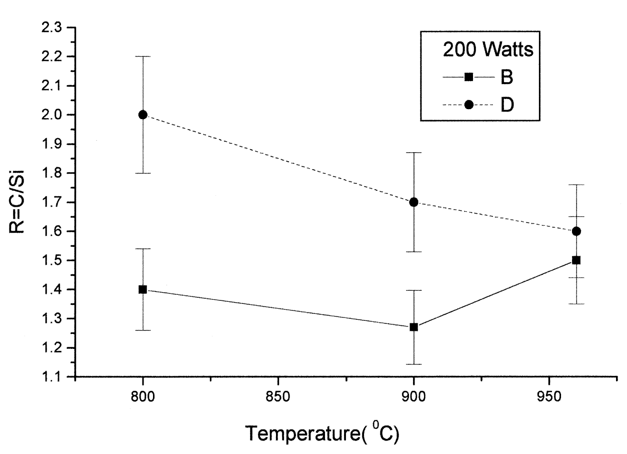

Fig. 3. The variation of the sample composition vs. the substrate temperature for a plasma power of 200 W. The curves A and B are for the gas mixtures Ar/CH_4 of 80:20 and 70:30, respectively.

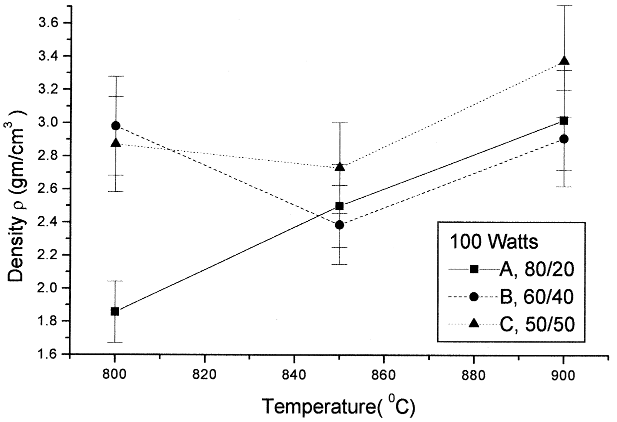

Fig. 4. The variation of the density of the deposit vs. the substrate temperature for a plasma power of 100 W. The curves A, B and C are for the gas mixtures Ar/CH_4 of 80:20, 60:40 and 50:50, respectively.

4. Discussion

This study has demonstrated various interesting aspects related to the preparation of a-SiC thin films prepared by the RF-RMS technique.

It is observed that the SiC film properties mostly depend upon the decomposition of CH_4 molecules and the bombardment-assisted chemical reactions on the surface of the Si target and on the substrate [6]. It has

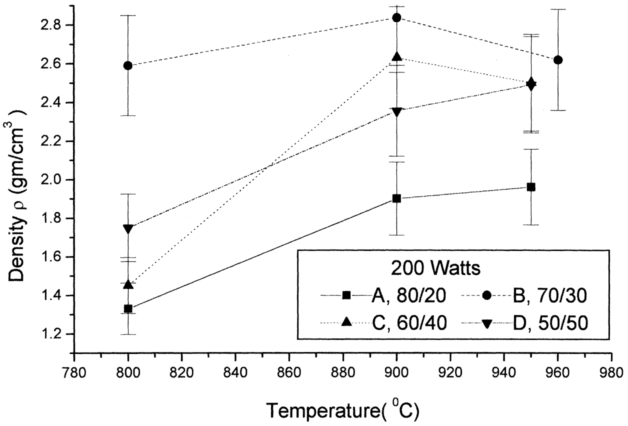

Fig. 5. The variation of the density of the deposit vs. the substrate temperature for a plasma power of 200 W. The curves A, B, C and D are for the gas mixtures Ar/CH_4 of 80:20, 70:30, 60:40 and 50:50, respectively.

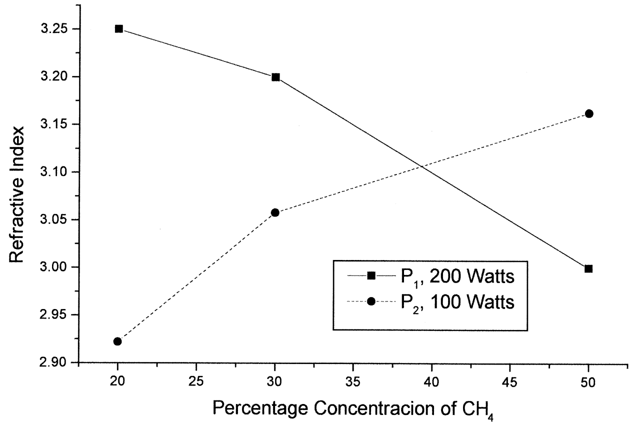

Fig. 6. The refractive index of the films as a function of the concentration of methane in the gas mixture.

been seen that the deposition rate and consequently the film properties largely depends upon RF power. The glow-discharge plasma conditions can be chosen in such a way that an intense decomposition of CH_4 molecules occurs in the magnetron plasma. The hydrocarbon fragments created in this manner are known to have a high sticking probability on the walls of the reaction chamber even without a concomitant flux of atoms (Si in this case) sputtered from the target. This implies that the consumption of the hydrocarbon gas will not only be dependent on the amount of the sputtered atoms, the pumping speed and pyrolysis on the heated substrate surface but also on the degree of decomposition in the plasma. The latter can be expected to play a crucial role in decreasing the temperatures. However, in order to obtain a detailed understanding of the mechanism of SiC film growth by the RMS technique, it is essential to understand the mechanism of plasma decomposition of the hydrocarbon molecules and their chemisorption behavior on the growing film surface.

DR is an important parameter which largely depends upon the decomposition of CH_4 molecules for the preparation of SiC films by RF-RMS technique. From the results, it is clearly found that DR is high for higher RF power which means that the decomposition of CH_4 molecules is high for higher power. However, the density curves show that at lower DR, high density SiC were obtained which is in good agreement with the bulk value of the density of the SiC (3.2 gm/cm^3). Moreover, at lower RF power stoichiometric films can be obtained at higher CH_4 concentration and at lower substrate temperature. This means that the decomposition of CH_4 molecules and the bombardment-assisted chemical reactions are sufficient to form good quality a-SiC films at lower RF power.

5. Conclusion

SiC films have been prepared by using the RF magnetron sputtering technique by changing the deposition parameters over a wide range and several characterization techniques have been used to optimize the quality of the films. It is to be concluded that DR is low but dense and stoichiometric a-SiC films can be obtained at lower RF power. This signifies that at lower RF power but higher CH_4 concentration, sufficient number of carbon radicals are formed and participate in the bombardment-assisted chemical reactions on the surface of the target and the substrate to form good quality SiC films.

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