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Laser annealing of sputter-deposited *a*-SiC and *a*-SiC_xN_y films

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Abstract. **This work describes the laser annealing of *a*-SiC and *a*-SiC_xN_y films deposited on (100) Si and quartz substrates by RF magnetron sputtering. Two samples of *a*-SiC_xN_y thin films were produced under different N_2/Ar flow ratios. Rutherford backscattering spectroscopy (RBS), Raman analysis and Fourier transform infrared spectrometry (FTIR) techniques were used to investigate the composition and bonding structure of as-deposited and laser annealed SiC and SiC_xN_y films.**

Keywords. **Silicon carbide; silicon carbonitride; amorphous films; sputtering; laser annealing.**

1. Introduction

Silicon carbide (SiC) thin films are promising materials for high temperature and high power applications, being considered a natural complement for silicon as the structural material in micro- and nano-electromechanical systems (MEMS and NEMS) (Oliveira and Carreno 2006), because of their mechanical stability at high temperatures and their extraordinary chemical inertness. *In situ* doping of SiC films have been studied extensively to produce materials with optimized electrical and optical properties (Huran *et al* 2004). In this doping technique, dopant atoms are introduced during growth of the film. Nitrogen is an important *n*-type dopant in SiC. The nitrogen donors are assumed to substitute carbon atom in the lattice (Henry *et al* 2005). Among the most used *in situ* doping techniques are chemical vapour deposition (CVD), plasma enhanced chemical vapour deposition (PECVD) and magnetron sputtering. CVD thin films are known to be excellent for hard and wear-resistant coatings (Blum *et al* 1999). However, the CVD process requires high-deposition temperatures which limits it applications in microelectronics. PECVD and sputtering are low temperature processes that present high deposition rates, high-purity films and excellent adhesion film-substrate (Costa and Camargo 2003; Fujihira *et al* 2003). In spite of these advantages, generally films produced at low temperature are amorphous. To overcome this problem, thermal or laser annealing is performed to induce crystallization of the films (Fernandez-Ramos *et al* 2003).

In recent years, Garcia and co-workers (2004) compared surface roughness, resistivity and X-ray diffraction pattern observed in *a*-Si and *a*-SiC films crystallized by laser annealing under similar conditions. The main conclusions of these researchers were: (i) laser annealing does not cause enough reduction of resistivity in SiC films, (ii) the energy density of the laser used in the study was not sufficiently high to reach the melting temperature of SiC, but the surface temperature reached was enough to induce crystallization, which was observed in XRD spectra and (iii) low energy density crystallization process improved the texture of the film surface.

Many researchers have performed studies comparing the effect of thermal and laser annealing on the properties of silicon alloys (Parr *et al* 2002; Sedky 2007). These studies reported laser/annealed films to have better device properties than thermal annealed. Moreover, laser recrystallization can yield large grains of silicon without long processing times or the requirement for the whole sample to be subjected to high temperatures (Czubatyj *et al* 1991). However, this technique presents high cost and poor material uniformity related to the inhomogeneous temperature distribution induced by a focussed laser beam (Yamada *et al* 1986; Yu *et al* 1995).

In our previous work, we show the effect of nitrogen doping and thermal annealing on structural properties of sputter-deposited *a*-SiC films (Fraga *et al* 2008). In this work, our objective is to investigate the correlation between nitrogen content in the film and structural modifications caused by laser annealing. In order to verify this correlation, Raman spectroscopy and Fourier transform infrared spectrometry (FTIR) techniques were utilized.

2. Experimental

Amorphous SiC and SiC_xN_y films were grown by RF (13·56 MHz) magnetron sputtering of a SiC target (99·5%

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Table 1. Deposition conditions of SiC and SiC_xN_y thin films by RF magentron sputtering.

	Parameters						
Sample	Target	Ar flow (sccm)	N_2 flow (sccm)	RF power (W)	Working pressure (Torr)	Target-substrate distance (mm)	Deposition time (min)
N0	SiC	7·0	–	200	2×10^{-6}	75	120
N1	SiC	7·0	0·7	200	2×10^{-6}	75	120
N2	SiC	7·0	1·4	200	2×10^{-6}	75	120

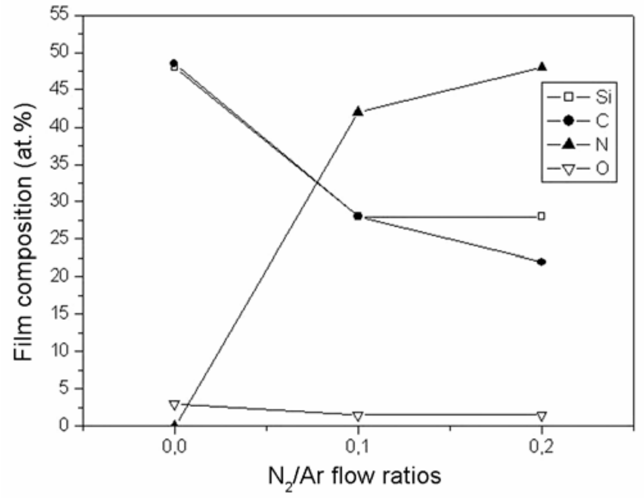

Figure 1. Film composition as a function of N_2/Ar flow ratio during deposition process.

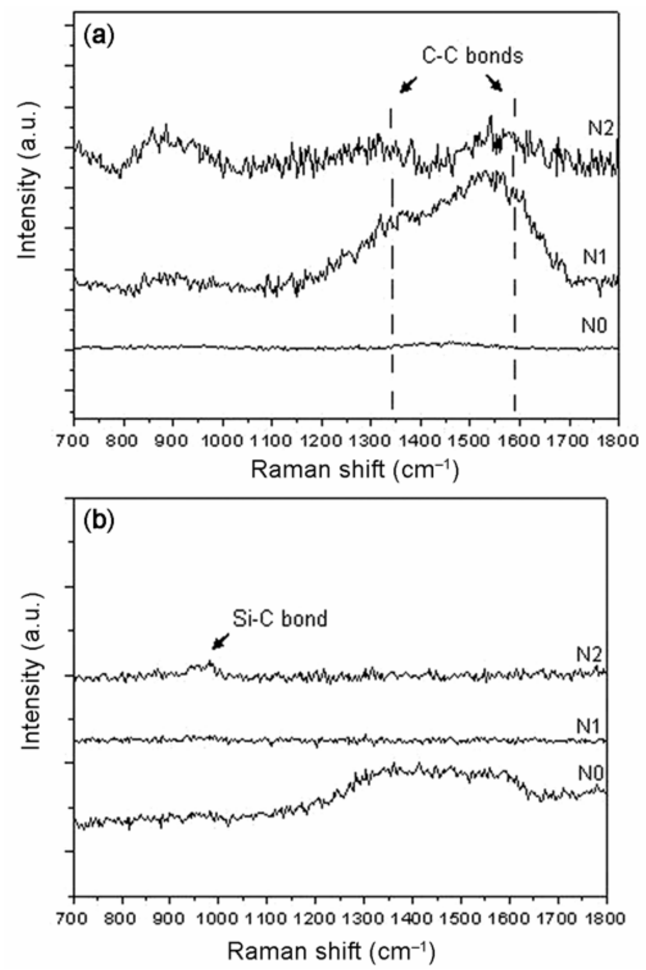

Figure 2. Raman spectra of SiC film (sample N0) and SiC_xN_y deposited at different N_2/Ar flow ratios: (**a**) as-deposited and (**b**) laser annealed.

purity) in Ar + N_2 atmosphere. Table 1 summarizes deposition conditions. The films were simultaneously deposited on silicon and quartz substrates. The quartz substrate was used because a transparent substrate will not be subjected to significant undesired heating by the laser light. The silicon and quartz substrates were cleaned by standard RCA procedures and 5 : 1 : 1 $H_2O : H_2O_2 : NH_4OH$ solution, respectively. In order to crystallize the *a*-SiC_xN_y films, laser annealing was performed by scanning Cu–HBr laser beam over the surface of the films. The specimen was mounted on a platform with three degrees of freedom, capable of planar translational and rotational motions. The platform is fully programmable and its speed, position and line spacing can be accurately controlled. A CAD program was used to define repeatable and reconfigurable annealing patterns. In the experiments, laser power was fixed at 4·3 W and the scan speed was varied from 10–100 cm/s. All scans were performed in air at room temperature.

RBS measurements were performed using a beam of 2·2 MeV He^+ and scattering angle of 170°. Raman analysis was performed with a Renishaw 2000 system using an Ar^+-ion laser ($\lambda = 514$ nm). The laser power on the sample was ~ 0·6 mW and the laser spot had a 2·5 μm diameter. Infrared spectra in the 400–4000 cm^{-1} wavenumber range were acquired using a Perkin Elmer spectrum 2000 Fourier transform infrared spectrometer. A (100) silicon wafer was used as reference.

3. Results and discussion

RBS measurements were used to determine composition of the films. The RBS spectra were analysed with the help of a simulation software RUMP (Dolittle 1986). Figure 1 shows composition of the film as a function of N_2/Ar flow ratios. It was observed that the film deposited without nitrogen is a stoichiometric compound of Si and C. It also can be observed that the carbon content in the film decreases as a function of N_2/Ar flow ratio increases. All samples present small amounts of oxygen (~ 2%). This contamination of the film might have occurred either by the exposure of the samples to air or by oxygen contamination of the sputtering system.

In this study, Raman and FTIR analysis have been used to observe the following effects: nitrogen addition on the structure of the SiC film and their structural modifications induced by laser annealing. Figure 2 shows Raman spectra of as-deposited and laser annealed films. Raman analysis of *a*-SiC film (sample N0) does not present evidences of any peak corresponding to C–C bonds. The *a*-SiC$_x$N$_y$ films show bands, centred around 1350 cm^{-1} and 1580 cm^{-1} and a relatively weaker band around 830 cm^{-1} which corresponds to C–C bond and Si–C bond, respectively. After laser annealing, SiC film (sample N0) clearly shows C–C bonds at 1330 and 1595 cm^{-1}, corresponding to sp^2 and sp^3, respectively. On the other hand, Raman spectrum of sample N1 does not present peaks or bands that indicate the presence of C–C, Si–C or Si–N bonds. For sample N2, only a peak corresponding to Si–C bond (970 cm^{-1}) was observed.

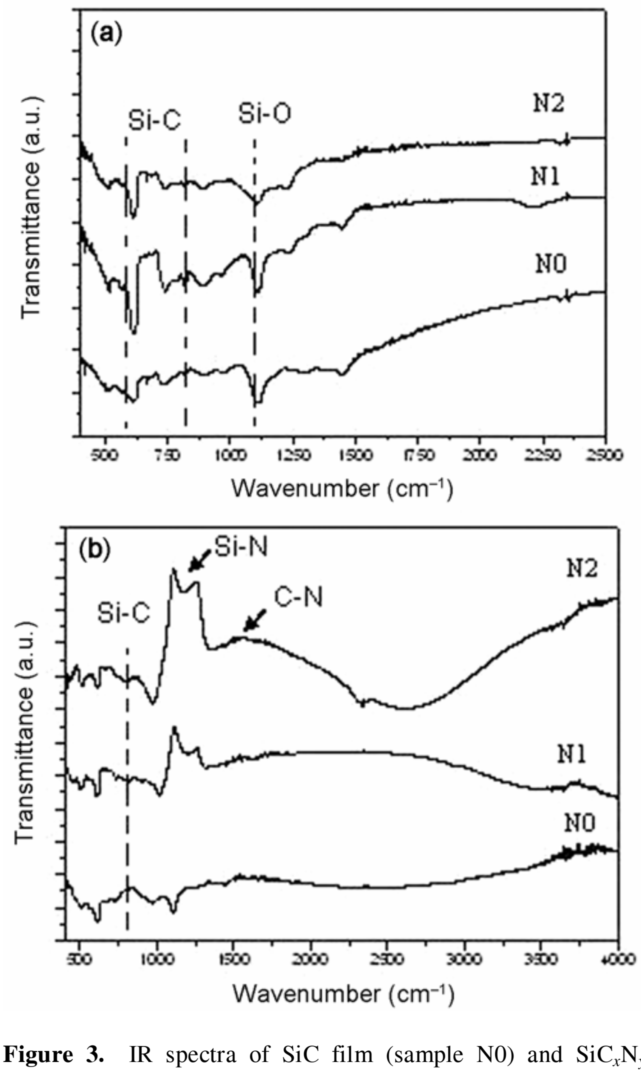

Figure 3. IR spectra of SiC film (sample N0) and SiC$_x$N$_y$ deposited at different N$_2$/Ar flow ratios: (**a**) as-deposited and (**b**) laser annealed.

Additional information about Si–C, C–C, Si–N and C–N bonds can be obtained from IR transmission spectra of the as-deposited and laser annealed films as shown in figure 3. For stoichiometric as-deposited SiC film (sample N0), transmission peaks associated to the Si–C (~ 607, ~ 841 cm^{-1}) and Si–O (~ 1108 cm^{-1}) bonds was observed. These bonds were also observed in the samples of SiC$_x$N$_y$ films (samples N1 and N2). FTIR spectra of all samples, after laser annealing, exhibit Si–C peaks position from 611–620 cm^{-1} and from 844–870 cm^{-1}. A peak associated to Si–O bond (~ 1108 cm^{-1}) was also observed. IR spectrum of sample N2 indicates the formation of Si–N (~ 1035 cm^{-1}) and C–N (~ 1345 cm^{-1}) bonds.

4. Conclusions

In summary, laser annealing was carried out on sputter-deposited *a*-SiC and *a*-SiC$_x$N$_y$ thin films using Cu–HBr laser. Films with different composition were deposited on Si and quartz substrates under different N$_2$/Ar flow ratios. No significant differences were observed among the structural properties of the films deposited on Si and quartz. RBS measurements indicate that carbon content in the films decreases with the increase of N$_2$/Ar flow ratios. The results of FTIR and Raman analysis of as-deposited and laser annealed films show structural modifications induced by laser annealing.

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