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LARGE-AREA PULSED LASER DEPOSITION OF SILICON CARBIDE FILMS

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ABSTRACT

Silicon carbide (SiC) thin films are attractive for a wide range of applications from microelectronic and opto-electronic devices to protective and tribological coatings. In this paper, we will demonstrate that silicon carbide films can be successfully deposited by pulsed laser deposition (PLD) technique over large areas, with good uniformity in thickness, composition, structure and optical properties.

Amorphous SiC films were grown on silicon wafers of 75-mm diameter over a temperature range of 25 – 650 °C using a KrF excimer laser at a wavelength 248 nm and a repetition rate of 100 Hz. The large-area uniform coverage was obtained by rastering the laser beam over the radius of a rotating SiC target of 90-mm diameter, while the substrate was rotated simultaneously. The uniformity of film composition over the 75-mm wafers was characterized by Auger electron spectroscopy (AES), while the crystallinity of films was investigated by X-ray diffraction (XRD). The morphology of the films was evaluated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thickness and the index of refraction of coatings along the wafer radii were measured optically using a spectrophotometer.

INTRODUCTION

SiC is the material of choice for the production of electronic devices that can be used in conditions of high temperature, high frequency, high power and high irradiation [1-3]. This is due to its excellent physical and electrical properties, such as wide bandgap, high electric breakdown field, high thermal conductivity and high-saturated electron drift velocity. The wide bandgap of SiC material is promising for certain applications, such as the use in light-emitting diodes [4]. The high electric breakdown field provides the possibility for a SiC RAM to hold its charge indefinitely [1]. The excellent mechanical properties, such as its hardness and wear resistance, are attractive for protective and tribological coatings [5]. Its stiffness and radiation hardness make SiC the material of choice as X-ray masks in X-ray lithography [6]. SiC also has the potential to replace the rare earth dielectrics such as Gd_2O_3 in microelectronic devices [7]. The combination of excellent electrical, mechanical and chemical properties makes SiC a material well suited to replace Si for microelectromechanical systems (MEMS) working in harsh environments [8].

Chemical vapor deposition (CVD) is the most common technique for growing epitaxial SiC films. The deposition temperature for epitaxial growth of SiC films is usually above 1200 °C for atmospheric pressure CVD and 1000 °C for low-pressure CVD [8]. Other techniques, such as reactive sputtering [9] and molecular beam epitaxy (MBE) [10] have also been used to grow epitaxial SiC films at relative low deposition temperatures. Deposition conditions for growing polycrystalline and amorphous SiC films have fewer restrictions than those for epitaxial films. Therefore, numerous deposition methods, such as sputtering, reactive sputtering, reactive evaporation, and chemical vapor deposition and its variations [8], can be used. The films deposited by CVD technique usually contain hydrogen and, in addition, have difficulty to obtain good stoichiometric composition [11]. In order to have good mechanical properties, SiC films should be hydrogen-free and contain high density of covalent Si-C bonds [12]. PLD is a powerful technique to deposit hydrogen-free and stoichometric SiC films, either amorphous or polycrystalline [11-14]. PLD of a SiC target in vacuum could produce both neutral and ionized species with kinetic energies in the range of 10 –100 eV within the vapor plume [15]. Such high kinetic energies of ablated species are able to promote surface diffusion, nucleation, chemical bonding and high sticking probability. Therefore, the PLD technique is able to grow high quality stoichiometric SiC films at relative low temperatures. On silicon substrates, polycrystalline films can be produced at a substrate temperature of 800 °C [1], while epitaxial films can be grown at a deposition temperature of 1050 °C [16]. However, all reported work we found on the deposition of SiC films with PLD has been performed with simple approaches that led to the synthesis of films with good properties and acceptable uniformity only over small areas. The scale-up of PLD, to allow the deposition of coatings over large areas with uniform properties and thickness, is essential for using the PLD technique to manufacture SiC films.

In this article, we will present our work on the deposition of SiC films on 75 mm diameter silicon wafers by KrF excimer laser ablation of a SiC target in vacuum. Results on the uniformity of the thickness, composition, structure, and optical properties of the coatings will be presented.

EXPERIMENT

A schematic diagram of our large-area PLD system is shown in Figure 1. Detailed information about our PLD system has been described in previous publication [17]. The SiC films were deposited by ablating a 90 mm diameter rotating SiC target (stoichiometric, 99.5%) in an advanced vacuum chamber by means of a pulsed KrF excimer laser ($\lambda = 248$ nm), at a repetition rate of 100 Hz. To achieve uniform deposition over the entire substrate surface, the laser beam was rastered over the left-side radius of the rotating target. A programmable kinematic mount was used to control the rastering movement of the last mirror in the optical train.

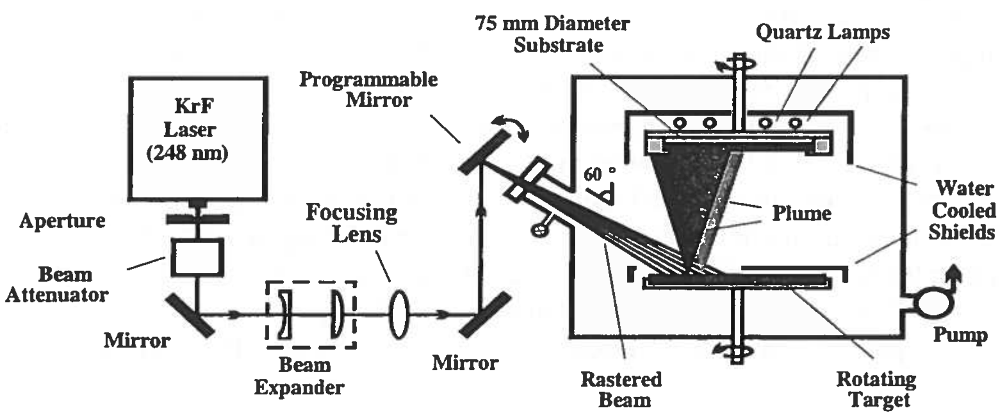

Figure 1: Schematic of the large-area PLD setup.

A 75 mm diameter silicon wafer (p-type Si<100>, $\rho = 10\text{-}30\ \Omega$.cm) was used as a substrate for PLD of the SiC film. Before introducing a wafer into the deposition chamber, it was cleaned by HF according to the procedure that was described previously [17]. After loading, the process chamber was pumped down below 2×10^{-6} Torr using a turbo-molecular pump. A blackbody-type heater that used quartz lamps on the top of the wafer, allows non-contact, radiation-based heating. When the temperature reached the preset value, the laser was then turned on and a pre-cleaning cycle of the target was performed for two minutes. Subsequently, the shutter that hid the substrate surface from the ablation plume was opened and the deposition started. After a given processing time, the laser was stopped and the substrate was allowed to cool down under vacuum. In the present experiments, substrates were heated up to 250 °C, 450 °C, and 650 °C, respectively. The on-target laser beam fluence was adjusted to about 2 ~ 3 J/cm^2.

The morphology of the PLD films was investigated by scanning electron microscopy (SEM, *Hitachi*, S-570) and atomic force microscopy (AFM, *Digital Instruments*, Nanoscope III). Depth-profiling by Auger electron spectroscopy (AES, *Perkin-ElmerPhysical Electronics Single-pass CMA Auger Spectrometer*; 3 keV Ar^+ sputter beam at 60° off-normal) was used to investigate the homogeneity of the film composition throughout the whole wafer. The derivative spectra of the C_{KLL}, Si_{KLL} and O_{KLL} lines were used to determine the atomic concentrations. The sensitivity factors used in the AES investigations were obtained from the analysis of SiC powder taken from the target used for the ablation. The structure of the SiC films deposited at various temperatures was examined by X-ray diffraction (XRD, *Philips*, X-Pert MRD) in the θ_0-2θ thin film configuration, where θ_0 was fixed at a value of 1°. The composition and structure were examined at 5 locations of the substrates (Figure 2-a) to evaluate the uniformity of the structure and composition of the films. The thickness, refractive index and extinction coefficient were simultaneously evaluated at a number of locations (Figure 2-b) across the whole wafer by spectral reflectance in the 250-850 nm ranges using a fiber-optic-based spectrophotometer (*Scientific Computing International*, Film Tek 3000). A generalized Lorentz oscillator model, developed by SCI, was used for curve fitting.

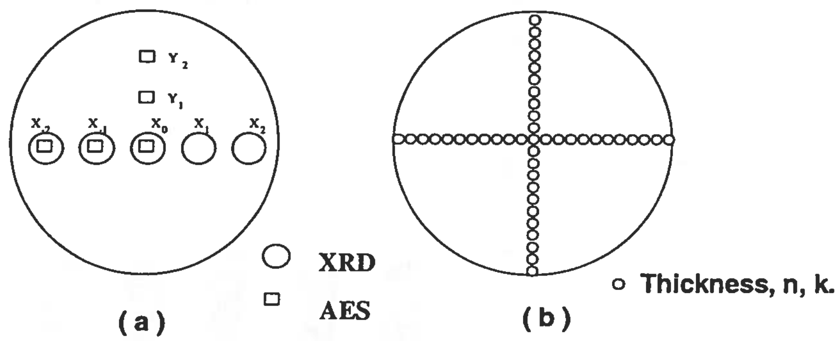

Figure 2: Layout of the probing locations over the 75 mm diameter wafers to investigate the uniformity of the films in terms of (a) composition and structure, and (b) thickness and optical properties.

RESULTS

The surface morphology of a SiC film deposited at a temperature of 450 °C is shown in Figure 3. A dense and smooth surface was obtained, with the occasional inclusion of spherical particles with diameters typically in the range 0.1 - 0.3 µm. Such particles were generated during laser ablation of the SiC target and became a characteristic of the PLD technique [18]. AFM imagining reveals that the SiC film deposited at 450 °C has a very smooth surface with an rms surface roughness of approximately 0.28 nm as shown in Figure 4. No significant difference in morphology was found for the SiC films deposited within the temperature range of 25 - 650 °C.

The normalized thickness of a SiC film deposited at the temperature of 450 °C was measured by a spectral reflectance technique along the radial position across the wafer and presented in Figure 5. The PLD SiC thin film is very uniform with an average thickness deviation across the

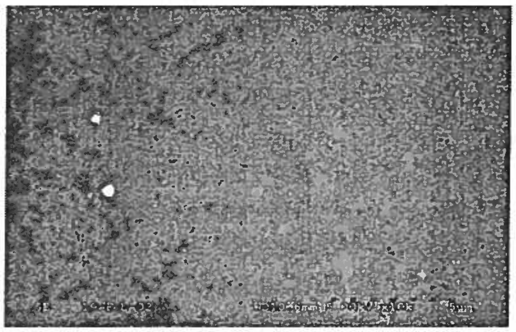

Figure 3: SEM micrographs of a SiC film deposited at a substrate temperature of 450 °C. Magnification: ×10,000, Film thickness: 62 nm.

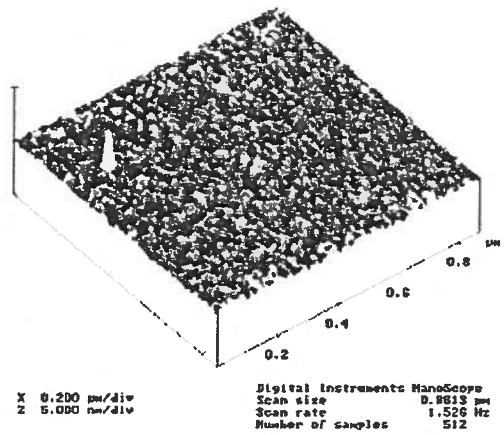

Figure 4: AFM imagine of SiC film deposited at a substrate temperature of 450 °C. The film thickness is 335 nm.

wafers below 0.5%. For a SiC film deposited at a temperature of 450 °C, the atomic concentrations of Si, C and O were determined by AES depth profile at different locations across the wafer (Figure 6). The nearly stoichiometric SiC film has very uniform composition distribution with average deviations of less than 0.5 % in atomic concentration of Si, C and O. The AES depth profile investigations also revealed that the Si and C concentrations were uniform throughout the bulk of the films, while the atomic concentration of O contamination decreases with increase in the sputtering time.

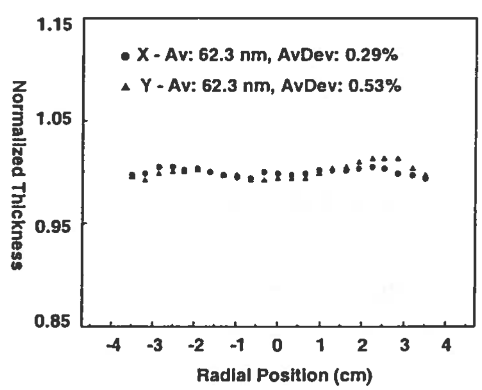

Figure 5: Normalized thickness of SiC films as a function of the radial position. Substrate temperature: 450 °C. Av: Average, AvDev: Average deviation.

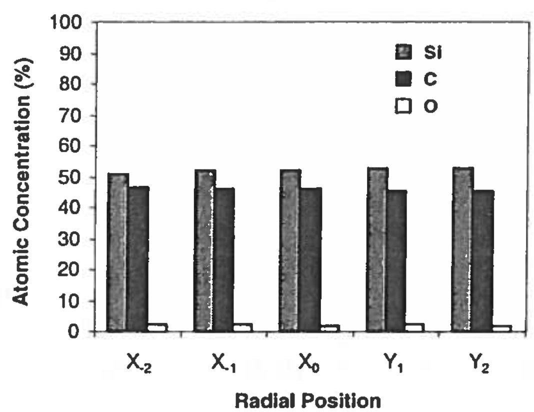

Figure 6: Si,C and O atomic concentration of SiC films as measured by AES at different locations of the Si wafer. Substrate temperature: 450 °C.

The dispersion of the index of refraction and extinction coefficient is presented in Figure 7. The dependence of the refractive index, n, on the radial position across the wafer is presented in Figure 8, for a deposition temperature of 450 °C. The index, n, is given for $\lambda = 633$ nm and its average values are n = 2.27. Such a high n value is indicative of highly packed, dense film.

Figure 9 presents the XRD spectra of SiC films deposited at different substrate temperatures. For all the substrate temperatures, the diffraction pattern consisted of a diffuse-scattering curve

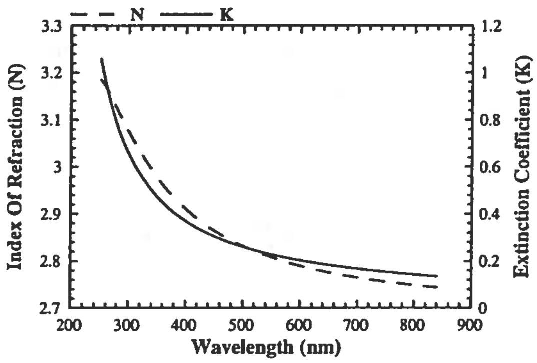

Figure 7: Dispersion curves of the index of refraction, n, and extinction coefficient, k, of a SiC film deposited at 450 °C.

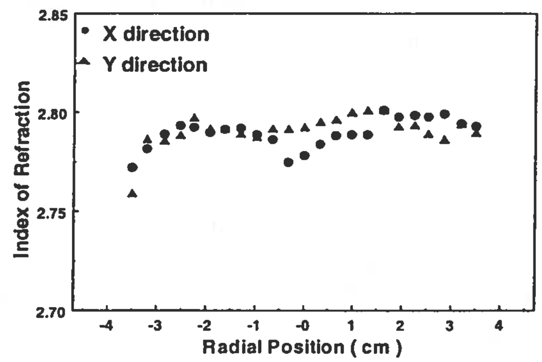

Figure 8 : Radial profile of the index refraction, n, of a SiC film deposited at 450 °C.

with a broad band centered at 2θ of about 32°. Such a profile indicates an amorphous-like structure. The broad band grows as the substrate temperature increases, which indicates that more textured structure was formed at higher temperatures. XRD spectra were also taken at five different locations (Figure 2-a) on the wafers that were coated with SiC film at various temperatures. The XRD spectra at the different locations are identical to the curve at Figure 9 and indicate structure uniformity across the whole wafer for all processing temperatures tested (RT - 650 °C). Figure 10 shows the dependence of the refractive index and extinction coefficient of SiC films on the substrate temperatures at a wavelength $\lambda = 633$ nm. The index of refraction as well as extinction coefficient decreased with increasing substrate temperatures. The decrease of the index of refraction might be attributed to a decrease in the density of the films as the substrate temperatures increase.

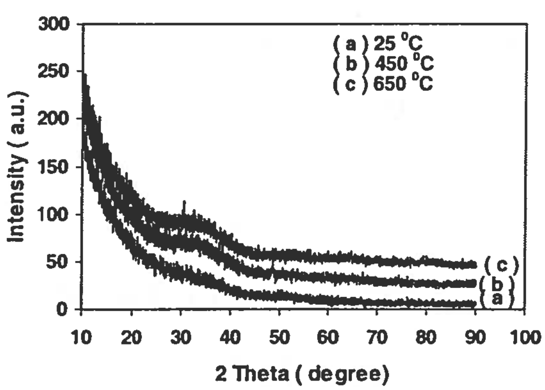

Figure 9: XRD spectra of SiC films deposited at (a) 25 °C, (b) 450 °C and (c) 650 °C.

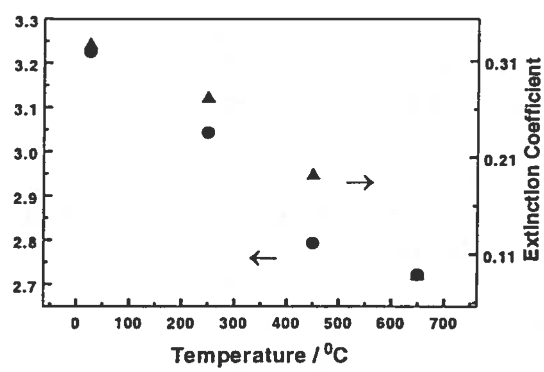

Figure 10: Dependence of n and k of the SiC films on the deposition temperatures. Values of n and k are given for $\lambda = 633$ nm.

CONCLUSIONS

Large-area amorphous SiC films were successfully deposited by laser ablation in vacuum, at temperatures up to 650 °C. Excellent uniformity was achieved in terms of composition, structure, thickness and optical properties across 75 mm diameter silicon wafers. The experimental results demonstrate that PLD is suitable for the production of large-area homogeneous SiC coatings, with superior optical properties.

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