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AES Studies of Heteroepitaxial SiC Films Deposited on Si and on Sapphire Substrates by MOCVD

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Abstract

Auger electron spectroscopy (AES) has been used to investigate the chemical composition of the heteroepitaxial silicon carbide films grown on Si (100) and sapphire (0001) substrates at 900 °C by the MOCVD technique using DEMS precursor. Auger spectra were obtained from the surface and as a function of depth of 2 micron thick SiC films. AES measurements were performed under very high vacuum 10^{-9} Torr conditions. Surface cleaning and depth profile studies were carried out by using Ar^+ ion beam sputtering. Auger spectra of the surface indicate Si LVV, C KLL and O KLL peaks. The Si LVV signals on the 'as prepared' surfaces for both substrates indicated that the silicon was in the oxide state, which was removed after 15 min Ar^+ ion cleaning. Depth profile studies showed, that after 20 min of ion cleaning the SiC films possess near stoichiometric composition. Moreover, the C KLL signal on the ion cleaned films showed the carbon in the carbide state. X-ray diffraction analysis of the SiC films on the sapphire (0001) and Si(100) substrates has shown a high intensity single peaks at 35.7º, which indicates the presence of SiC at orientation (111).

Introduction

Silicon carbide is a wide bandgap semiconductor material with high breakdown electric field strength, high saturated drift velocity of electrons, and a high thermal conductivity [1-3]. Also, SiC is a very hard material with a Young's modulus of 424 GPa [4] and it is chemically inert. All these properties can be used to create a new generation of devices that can operate at high-power, high-frequency, high-temperature, radiation, and chemical aggressive conditions. SiC is also used as substrate for LEDs made from GaN, which is the largest market of semiconductor-grade SiC and also, as high temperature gas sensors [5]. However, the small size of the substrate and the high production cost put restrictions for uses of SiC-based devices. Monocrystalline silicon carbide heteroepitaxial films deposited on cheap substrates can greatly reduce the cost of the substrate and increase their size.

Auger electron spectroscopy has been used to analyze the chemical composition of the surface and depth profile layers of SiC films. Auger spectra provide information about the elemental composition and chemical compound of the SiC films. The degree of oxidation of the surface can also be studied by Auger spectroscopy. Measuring the depth profile of the sample allows one to obtain data on changes in the composition of the material along the film thickness. SiC monocrystalline wafers have been previously investigated by AES [6-7]. Also, hetero-epitaxial silicon carbide films on silicon obtained by RF-sputtering technique were studied [8].

In the present work the composition as a function of depth of SiC films was investigated by removing layers by ion bombardment (sputtering). Ion bombardment is a very useful technique for modifying, cleaning and sputtering solid state surfaces, especially for producing materials with high resistance against chemical environments. In addition, the use of argon or other noble gases makes the technique environmentally clean, because of the absence of poison gases in the technological process. Sputtering yields of SiC under Ar^+ bombardment and sputtering angles were determined in work [9].

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Experimental

SiC films were grown by MOCVD on sapphire (0001) and Si (111) substrates in a custom made vertical stainless-steel vacuum chamber. Films were synthesized at 900 ºC using diethylmethylsilane (DEMS) as a single precursor without any carrier or bubbler gas, under a pressure in the chamber 5×10^{-5} Pascal [10]. SEM cross section images showed 2 micron thick SiC films on both Si and sapphire substrates. Surface elemental and chemical compound analyses were investigated by Auger electron spectroscopy (AES). A schematic diagram of the setup for Auger Electron Spectroscopy is shown in Fig. 1. Auger spectra were taken by PHI model 15-110 cylindrical mirror analyzer. Primary electron beam energy was 3 kV with an emission current of 15 mA. Samples were mounted on the PHI Model 15-600 Specimen stage carrousel sample holder with a manipulator which could move the samples in the x, y and z-directions. The AES measurements were performed under very high vacuum (10^{-9} Torr) which was obtained by an ion pump to eliminate surface contamination or oxidation of the samples. For this reason, the vacuum chamber was put through several dry pumping procedures including baking. Also, mass spectrometry was used for the gas analysis in the chamber. The Auger chamber was equipped with a sputter ion gun to obtain depth profiles of the samples. As a sputtering gas source ultra-high purity Ar gas was used. Before depth profiling, the ion pump was valved off and the chamber switched to a turbo molecular pump and argon gas was supplied to the chamber through a leak valve until a pressure of 5×10^{-5} Torr was reached. The surface was sputtered eroded by an Ar^+ ion beam with energy 3 kV. AES spectra were measured during sputter erosion to yield depth profiles of the grown SiC films. The sputtering time between each AES measurement was 5 minutes. After the sputtering of the samples was completed, the vacuum chamber evacuated. Auger electron energies were scanned from 25 to 600 eV to identify the Auger peaks of Si LVV, C KLL and O KLL.

Atomic structure of the heteroepitaxial SiC films was investigated X-ray analysis with a Siemens D5000 X-Ray Diffractometer. The X-ray scans were done in the standard θ-2θ configuration, using Cu K_α radiation of wavelength 1.54 Å at 30 mA and 40 kV with a scan step of 0.05º. The XRD of substrates has identified 2θ - 69º for (100) plane Si and 2θ - 41.8º for (0001) plane sapphire single crystals.

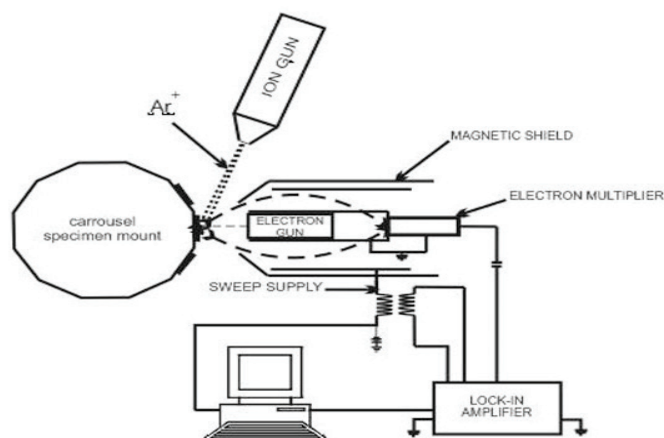

Fig. 1. Schematic setup for Auger electron spectroscopy.

Results and Discussions

The AES spectra of the surface and as a function of depth of the film deposited on the sapphire substrate at 900ºC by MOCVD are shown in Fig. 2. The sputtering time between curves 1-5 was 5 min while it was 10 minutes of sputtering time between the other AES spectra. Auger spectra of the SiC films deposited at 900ºC show almost the same peak structures on both substrates during the depth profiling until 20 minutes sputtering time. The AES spectra for both SiC films showed the Si LVV peak at 78 eV, the C KLL peak at 272 eV and the O KLL peak at 503 eV, which indicate that the surfaces of the films ha a silicon oxide layer contaminated with graphitic carbon. Other elements on the surface are not detected. After 5 minutes of sputtering (Fig. 2 - curve 2) the surface shows the carbon and oxygen peaks decreased without signal shifts and the silicon peak is shifted to a pure silicon position.

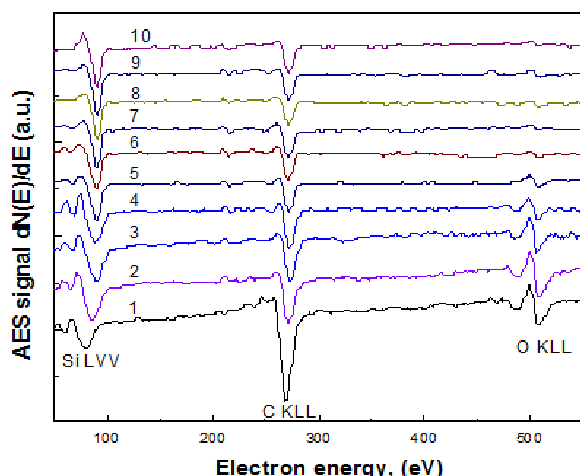

Fig. 2. Auger spectra of a SiC film on Si (100). The sputtering time 1 - surface, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 20 min, 6 - 30 min, 7 - 40 min, 8 - 50 min, 9 - 60 min, 10 - 70 min

This composition change can be explained by destruction of Si-O bonds at the high ion energes makes for formation of Si-Si bonds and desorption of free oxigen atoms from the oxide layer, which can react with carbon contamination under the high energies to form CO or CO_2 gases [11]. After 10 minutes of Ar sputtering it is seen that the silicon peak has increased and moved to the pure Si LVV value of 92 eV [12]. Also, the AES spectrum shows an argon peak due to implantation of the argon ions used for sputtering. After about 20 minutes of sputtering the O KLL peak has almost disappeared, and the C KLL peak has decreased to nearly the stoichiometric ratio of SiC. Figure 3 shows the magnified Si LVV peaks of SiC films deposited on Si and sapphire substrates. Auger spectra are shown for the surface and for the film after 5, 10, 15 and 20 min of argon ion sputtering. Figure 3 shows that from the surface to 15 min sputtering time the Si LVV peaks of SiC films change from oxide state value of 78 eV to that of pure silicon at 92 eV.

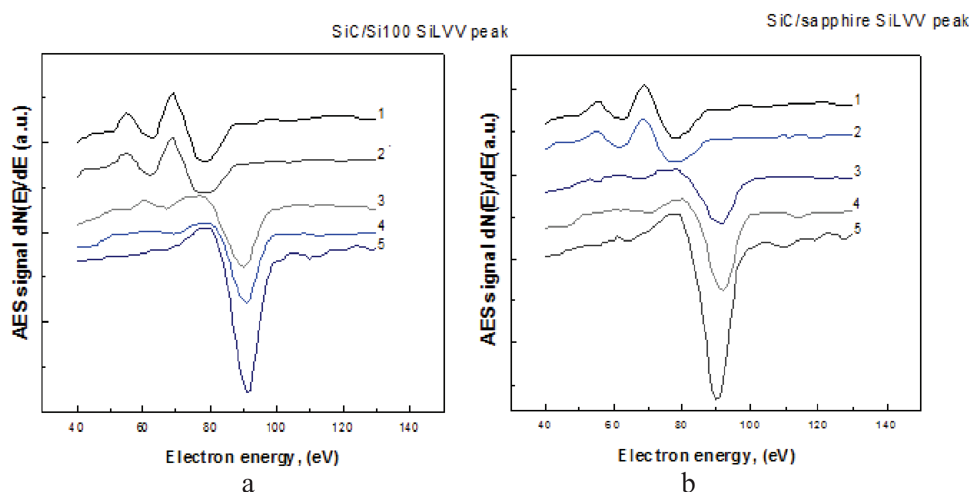

Fig. 3. Magnified Si LVV peaks of SiC films deposited on Si (a) and substrate sapphire substrates (b). The sputtering time 1 - surface, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 70 min.

However, after 20 min sputtering time the Si LVV peak of the SiC film on Si substrate has moved to 91 eV, and of the SiC film on sapphire the Si LVV has moved to 90 eV. The magnified C KLL peaks of the SiC films deposited on Si and sapphire substrates are shown in Fig. 4 (a, b). It can be seen that the line shape of the C KLL signal on both films is quite similar. Carbide type Auger peaks in the spectra seen only in curve 5 of Fig. 4 are labeled A1, A2 and are located before the main carbon peak [13]. In our evaluation 20 min of argon ion sputtering leads to an AES spectrum from a relatively clean surface, which gives the possibility for calculation of the stoichiometry between Si LVV and C KLL peaks. From the AES spectra and using tabulated sensitivity factors, we calculate the composition profile of the deposited SiC film by using equation:

$$C_a = \frac{I_a / S_a}{\Sigma I_i / S_i}$$

where, C_a is the atomic concentration, Ia is the peak to peak height of the differentiated Auger peak from element «a», and S_a is the relative sensitivity factor for element «a». The index «i» is a summation index for the elements included in the quantification.

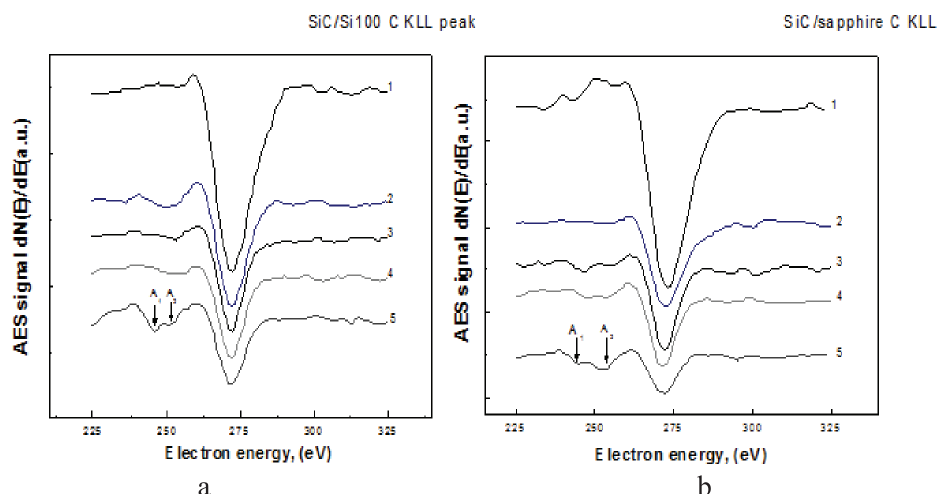

Fig. 4. Magnified C KLL peaks of SiC film deposited on Si (100) (a) and sapphire (0001) (b) substrates. The sputtering time 1 - surface, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 70 min.

Since measurements usually are performed on heterogeneous samples while the sensitivity factors are calculated from pure element standards there is generally some variation in the calculated composition ratios. Fig. 5 shows an Auger composition depth profile of the SiC film grown on Si (100). There is a large concentration of carbon near the surface, which indicates surface contamination 15 min of sputter cleaning reveals a fresh SiC surface, which is near stoichiometric SiC, as can be seen in Fig. 5.

The X-ray diffraction technique was employed to verify the phase and the orientation of deposited SiC films as well as to their lattice parameter. XRD scans were done between 10-90 of 2θ angle. Figure 6 shows the XRD spectra for SiC films deposited at 900OC on Si (111) and on sapphire (0001) substrates. An intense reflection peak of 3C-SiC (111) was observed at 2θ = 35.7°, indicating that the deposited β-SiC films have a single phase cubic structure on both Si (111) and sapphire (0001) substrates.

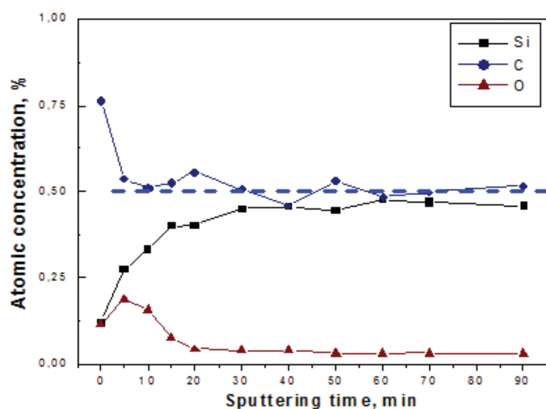

Fig. 5. Depth profile of SiC film deposited on Si (100) substrate at 900°C calculated by tabulated sensitivity factors.

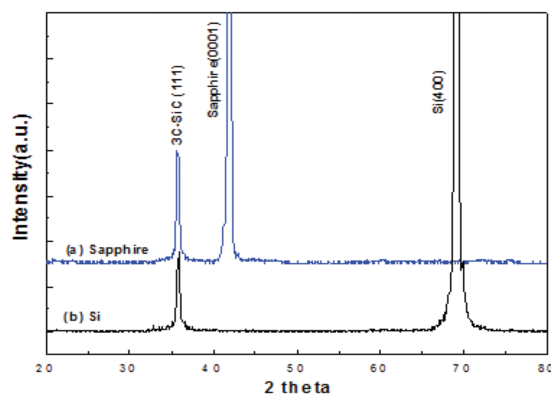

Fig. 6. XRD of thick SiC films deposited at 900 °C (a) on sapphire (0001) and (b) on Si (100).

The initial high concentration of oxygen in the AES data is mostly due to the SiC film's surface oxidation. The continuous weak oxygen signal principally comes from the background gases in the AES chamber. An argon signal is also observed, which is due to implantation of the argon ions from the sputtering beam used to do the depth profiling.

Conclusion

AES and XRD methods have been applied to studies of SiC films deposited on silicon and sapphire substrates at 900 °C by MOCVD technique. AES spectra showed that the deposition of films by MOCVD using a DEMS precursor resulted in the

stoichiometric silicon carbide epitaxially grown on (100) plane Si and (0001) plane sapphire substrates. The silicon LVV and the carbon KLL AES peaks showed that the films have carbide type chemical bonding structure. Depth profiling of the films showed a varying composition of oxygen and graphitic carbon contamination to finally a SiC composition after about 20 minutes of Ar^+ ion bombardment. The crystal structure of the SiC films deposited on both sapphire (0001) and Si (100) substrates as measured by XRD showed a single peak at 37.5º indicating the structure to be the SiC cubic polytype 3C-SiC along the (111) direction.

Acknowledgement

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