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Growth of crystalline SiC films under low electron temperatures in afterglow plasma region using triode plasma CVD

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Crystalline SiC films were grown at low temperatures by triode plasma CVD using dimethylchlorosilane diluted with hydrogen as a source gas. Dependence of the electron temperatures in discharge region and in afterglow region on the properties of SiC films such as crystallinity, chemical bonding structure and composition were investigated. Under negative grid bias condition, the electron temperature in the discharge region increased and that in the afterglow region became about one-tenth of that under positive bias condition. Corresponding to these variations, the crystallinity of SiC films was remarkably improved and the composition of the films became stoichiometrical. Under the negative grid bias, it is considered that the active high density hydrogen radicals were generated in the discharge region, diffused toward the substrate surface and extracted the weak bonds or excessive methyl groups from the film growing surface under low electron temperature. As a result of these processes, the SiC films with good crystallinity were grown.

1. INTRODUCTION

Silicon carbide (SiC) is an excellent widegap semiconductor material because of its thermal and chemical stability and large thermal conductivity. Due to ease of p-type and n-type doping, trial production of electronic devices operative at high-temperature and high-power[1,2] and of blue light emitting diodes[3-5] has been carried out. Moreover, it is expected as substrate for epitaxial growth of gallium nitride (GaN) because of the small lattice mismatch between SiC and GaN (3.4%)[6]. However, due to its high melting point, the crystal growth and epitaxial growth on substrates at low temperature ($\leqq$1000 ℃) are very difficult. High temperature growth more than 1000℃ gives rise to various problems such as redistribution of impurity atoms and incorporation of unexpected impurity. Then the realization of low temperature growth is desired earnestly.

In most cases, silane and hydrocarbon mixture has been used for SiC crystal film growth. However, a carefully designed safety deposition system is required because silane has pyrophoric nature. Therefore the search for novel monomers which are not flammable is significant for the growth of SiC films. Although the growth of cubic type SiC crystal films has been reported by low pressure chemical vapor deposition utilizing hexamethyldisilane which is a kind of organosilicon compound possessing the Si-C bonds in its molecule [7], the growth temperature is 1100℃. Further reduction of growth temperature is desired.

Employing reactive plasma process to synthesize the material which melting point is high and to decompose stable gases at low temperatures is very effective. On the other hand, the incidence of high energy charged particles on film growing surface is considered to prevent the growth of high quality crystal films. The control of electron temperature in conventional reactive plasma which, in most cases, is weakly ionized plasma is very difficult. Although the increase of plasma density (charged particle density in reactive plasma) is recognized by the increase of discharge power, that of electron temperature is scarcely observed. Then the selectivity of chemical reactions in the discharge region and on the film growing surface is hardly obtained. The films grow as a result of such diversified reaction processes. The control of plasma parameter such as electron and ion temperatures is essential for the growth of high quality crystal and for the fabrication of the next generation ULSI devices[8].

Inserting third electrode (grid) between cathode and anode of conventional capacitive coupled plasma reactor, discharge region can be confined between anode and grid. Substrate surface can be isolated from the discharge region using this configuration which is called triode plasma CVD apparatus[9]. Using the triode plasma CVD and applying the dc bias on the grid, it may possible to control the plasma density and electron temperature above and below grid electrode and to realize the growth of high quality crystal.

In this study, low temperature growth of crystalline SiC films by triode plasma CVD method was investigated using dimethylchlorosilane (DMC S) diluted with hydrogen as source gas. The influences of the grid bias on the plasma parameter in the discharge region and afterglow plasma region and on the properties of SiC films such as crystallinity, chemical bonding structure and composition were investigated.

2. EXPERIMENTAL

The triode plasma CVD system has a wire mesh electrode (grid) placed between the cathode and the anode of a conventional diode type rf plasma CVD chamber as shown in Fig.1. The grid (area=14 × 14cm^2, wire diameter=0.3mm, wire spacing=1.3mm) was connected to a dc electric source. Substrates were placed on the anode. Applying various dc biases on the grid, the confinement of rf plasma discharge above the grid and the control of impingement of the charged particles in the vicinity of the substrate surface were tried. The evaluation of plasma parameters such as electron temperatures and densities at the center of discharge region and at 4mm above the substrate surface were also carried out using double probe method.

Experimental conditions are as follows: rf frequency 13.56MHz, rf plasma power 100W, the distance between cathode and grid (d) 20mm, that between grid and substrate (L) 20mm, cathode diameter 85mm ϕ, DMCS gas pressure 0.1Torr, H_2 flow rate 10sccm, gas feed ratio DMCS/H_2=40~70, substrate temperature 470~480℃, dc bias applied to grid -100~100V, total gas pressure during deposition 270Pa. DMCS was spontaneously evaporated from a cylinder kept at 0℃. Film composition was measured by electron-probe microanalysis (EPMA). Chemical bonding structure of carbon atom was also evaluated using EPMA. The crystallinity of the films was measured by x-ray diffraction.

3. RESULTS AND DISCUSSION

The dependence of the electron temperatures and the electron densities measured at 10mm above the grid and 4mm above the substrate surface on the grid bias are shown in Fig. 2 and 3, respectively. The electron temperature in the center of the discharge region increases for both positive and negative biases. Although the electron temperature in after-glow plasma region, on the contrary, is about 4eV

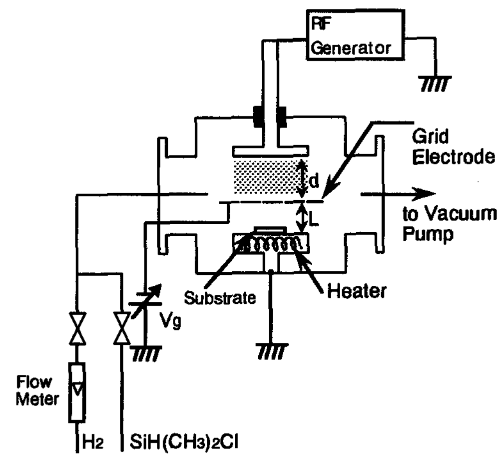

Fig.1 Schematic diagram of triode plasma CVD system.

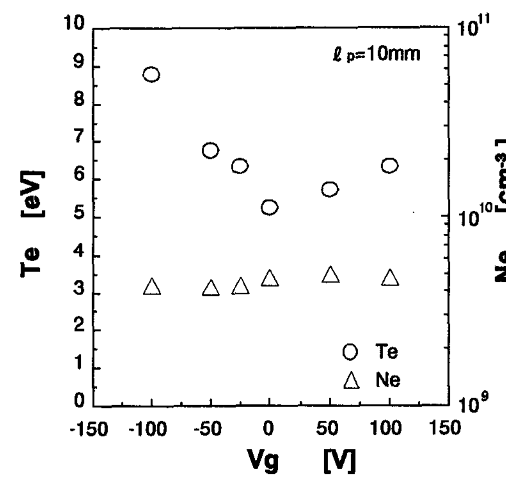

Fig. 2 Dependence of electron temperature and electron density at the center of plasma region on grid dc bias.

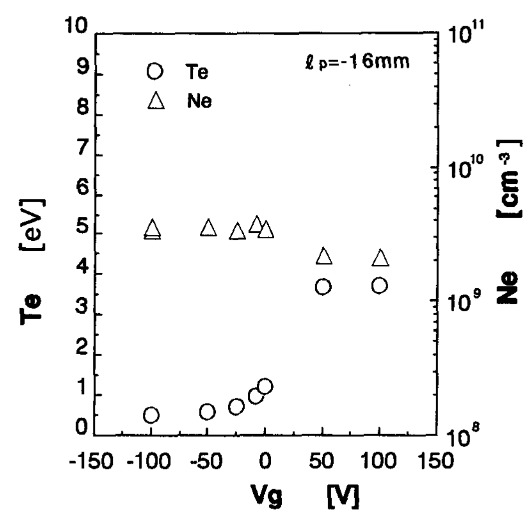

Fig.3 Depecdence of electron temperature and electron density at 4mm above anode on grid dc bias.

independent of the bias voltage under positive biases, it decreases to about 0.5eV under negative bias.

Under positive bias conditions, bright glow spreading out from discharge region to afterglow region below the grid could be observed with the naked eye. The vicinity of the substrate surface can be assumed to become active plasma condition under positive biases from the observation. Under negative bias conditions, the glow below the grid abruptly diminishes with increasing negative bias larger than 20V. The electron energy near the substrate surface can be understood to become small under negative bias. Under positive biases, space potential shifts to positive value. Positive ions can be accelerated to the anode ,which is grounded, by the potential difference between plasma space and anode. Then the glow can be considered to spread out below grid electrode. On the other hand, space potential under negative grid biases is lowered. As the electrons in the discharge region are effectively confined above the grid, electrons which possess large kinetic energy can only diffuse to the afterglow plasma region. During the diffusion, most of the kinetic energy was dissipated by the collision with molecules under high reaction pressure of 270Pa. As a result of these processes, the electron temperature in the vicinity of substrate surface was considered to lower more than one order.

The dependence of the residual stresses of SiC films on the grid bias is shown in Fig. 4. As can be seen in this figure, large compressive stress remains in SiC films prepared under positive bias conditions. The impingement of high energy positive ions from plasma space where potential is high to the substrate is suggested. On the other hand, the small tensile stresses are shown under negative biases. Due to low plasma potential under zero and positive bias conditions, the impingement of high energy ions is considered to be suppressed. Most of the tensile stress value is considered to be attributed to the difference of thermal expansion coefficient between Si substrates and SiC films. This variation corresponds to that of electron temperature in afterglow plasma region well.

Figure 5 shows the dependence of the crystallinity of SiC films on the grid bias. The crystallization was appreciably enhanced by the negative grid bias, while amorphous SiC films were grown under the positive dc bias. The FWHM value of diffraction peak became small as the negative bias increased. The diameter of crystalline particles is suggested to

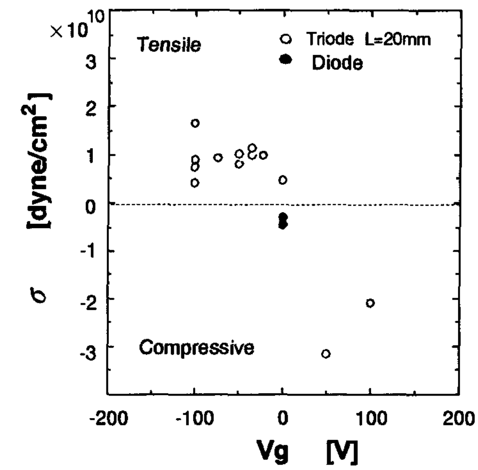

Fig. 4 Variation in the SiC film stress as a function of the grid bias. (Triode and diode plasma)

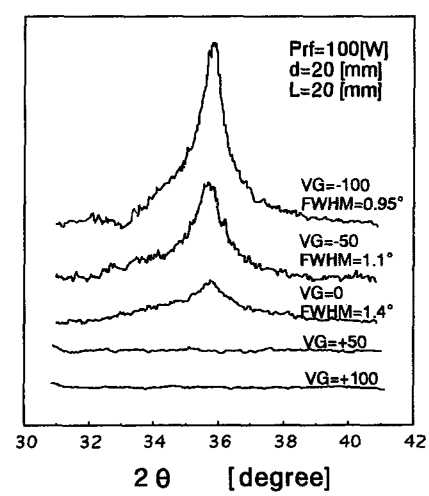

Fig. 5 Variation in the x-ray diffraction spectra for various grid biases.

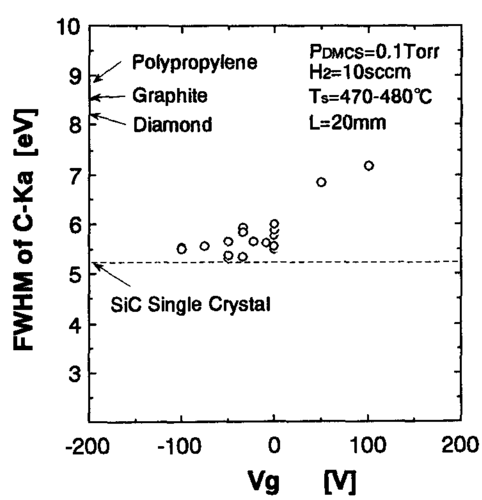

Fig. 6 Dependence of the FWHM values of C-Kα line on the grid bias. Anode is grounded.

become large under the bias. From these results, it is considered that the impingement of high energy ionic species hinders the crystallization of the SiC films. Under negative biases, the electron temperature in the discharge region became high. Then high density hydrogen radicals are considered to be generated and diffuse to the film growing surface. It is reported that hydrogen radicals anneal the film growing surface chemically and extract excess bonded hydrogens and methyl groups[10,11]. The relaxation of the film structure by such chemical annealing would enhance the crystallization.

The dependence of the grid bias on the FWHM of the C-Kα line is shown in Fig. 6. From the value of C-Kα line, the chemical bonding structure of carbon can be assumed[11]. Under zero and negative biases, the values of 5.3~5.5eV were obtained. These values are similar to that of crystalline SiC (5.25eV). On the other hand, FWHM value increases larger than 6.5eV with the positive grid bias. Many C-C bonds are considered to be incorporated in the SiC films under such conditions.

Under zero and negative bias conditions, SiC films with almost stoichiometry were obtained as shown in Fig. 7. The excess carbon atoms are considered to have been extracted from SiC films during film growth by the reactive hydrogen radicals as mentioned above. At grid bias of 100V, on the other hand, C/Si ratio exceed 2, which value is that of source gas (DMCS). The impingement of high energy ionic species would cause the incorporation of carbon atoms and/or the etching of the species containing Si atom. From these results, it can be found that the impingement of ionic species onto the film growing surface also hinders the role of hydrogen radicals which extract the excess carbon atoms (methyl groups) and also prevents the formation of the tetrahedral Si-C bonds.

4. Conclusions

In summary, the low temperature growth of SiC crystalline films by triode plasma CVD method was investigated using DMCS as source gas. The influences of the grid bias on the plasma parameter in the discharge region and afterglow plasma region and on the properties of SiC films such as crystallinity, chemical bonding structure and composition were also investigated. Under negative bias condition, the electron temperature in the afterglow region decreased to 0.5eV, while that in the discharge region increased up to 9eV. Under the condition, the proportion of tetrahedral Si-C bonds in SiC films increased and stoichiometrical crystalline SiC films were grown. Under negative bias, high density hydrogen radicals were generated in the discharge region and diffused to the film growing surface. Supplying high density hydrogen radicals onto static film growing surface, the precursors which contain carbon atom such as methyl groups were preferentially extracted and crystallization were consequently enhanced.

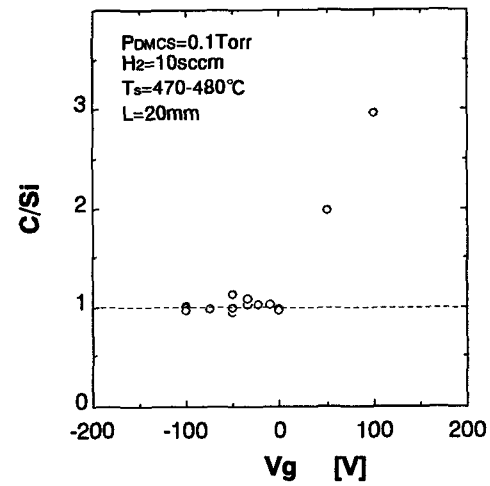

Fig. 7 Dependence of the C/Si ratios on the grid bias. Anode is grounded.

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