Laser Original

Effects of High-power Argon Excimer Laser Irradiation on Polycrystalline Silicon Carbide Mirrors

Masato OHMUKAI*, Hiroyoshi NAITO*, Masahiro OKUDA*
Kou KUROSAWA**, Wataru SASAKI**, Yasuo TAKIGAWA***
Tatsuhiko MATSUSHITA**** and Yoshiaki TSUNAWAKI****

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The effects of an argon excimer laser irradiation are studied on silicon carbide films which are deposited on sintered and pressed silicon carbide substrates by a low-pressure chemical vapor deposition (CVD) method. The SiC films consist of about 15 μm size crystallites highly oriented in such a way that the surfaces are parallel to (110). X-ray photoelectron and Raman scattering spectroscopic examination show that amorphous silicon is precipitated in the surface layers of silicon carbide films by the laser irradiation. The precipitation mechanism is discussed.

Key Words: Silicon carbide, Argon excimer laser, Laser mirror, Mirror damage, Silicon precipitation.

1. Introduction

In cooperation with the recent technological advance of silicon carbide (SiC) film fabrication, SiC is expected to be a suitable material for optical elements in the region of high photon energy such as vacuum ultraviolet (VUV) and X-ray radiation¹⁾. This stems from the fact that SiC has some desirable properties of high thermal conductivity and chemical inactivity. When SiC was used as mirrors for an argon excimer laser which has an ability to provide intense pulses at 126nm, we obtained the highest peak power of 16MW²⁾.

Through a series of these experiments, however, we found that the surfaces of some SiC mirrors undergo damages after the high

power operation³⁾. The origin of damage occurrence is not clear at present. It is therefore important to elucidate mechanism of the damage occurrence in SiC mirrors, in particular whether the damage occurrence is dependent on an inherent property of SiC or on the fabrication processes of the SiC mirrors.

Recently, a fabrication technique has been developed to prepare SiC films which consist of polycrystals highly oriented in such a way that the surfaces are parallel to a (110) crystallographic plane. In this paper, we report the radiation effects of a high power VUV laser on such polycrystalline SiC films. We examine SiC films by X-ray photoelectron spectroscopy (XPS) and Raman scattering measurements as well as a scanning electron microscopy (SEM). We

* Department of Electronics, University of Osaka Prefecture (Sakai, Osaka 593)

** Department of Electrical Engineering, University of Miyazaki (Miyazaki 889-21)

*** Department of Solid State Electronics, Osaka Electro-Communication University (Neyagawa, Osaka 572)

**** Department of Electronics, Osaka Sangyo University (Daito, Osaka 574)

discuss the mechanism of the surface modification by high power excimer laser irradiations. In addition we compare the present result with those reported previously.

2. Experimental

XPS spectra were taken with ESCA-1000 (Shimadzu) using the excitaiton radiation of Mg K α line, whose energy was 1254 eV. The analyzing chamber was evacuated to 5×10^{-7} Pa, and photoelectrons were introduced to a concentric hemispherical analyzer. The size of the analyzed area is 1 mm in diameter. The kinetic energy of detected photoelectrons was calibrated with Ag 3d line. The penetration depth of the VUV laser in SiC is about 5 nm, which is the same order as the analytical depth of XPS signals. An XPS is then suitable method to investigate the radiation-induced change of the film surfaces by VUV laser irradiation. All XPS spectra in this paper were obtained after the conventional smoothing⁴⁾ by 9 points and subtraction of linear backgrounds. Normally a Shirley background would have been used⁵⁾, but all the photoelectron peak of interest through this paper were situated on backgrounds so flat that there was no significant difference between the results of subtraction of each type.

We took Raman spectra at room temperature with NR-1000 Raman spectrometer (JASCO) in a quasi-backscattering configuration. An exciting light was a 514.5 nm line of an argon ion laser with a power of 300 mW. A 488.0 nm line was also used, but no significant difference was observed in both cases. The spectra taken with a 514.5 nm line are therefore presented throughout this paper. The analytical depths in SiC and Si are 3.5 μm and 680 nm respectively, which are estimated from the absorption coefficient of these materials at 514.5 nm. The polarization effects of incident and scattered lights were not

considered. The spot size of the incident light beam on sample surfaces was about 200 μm in diameter. The scattered light was analyzed using a double monochromator in conjunction with a conventional photon counting system in the wavenumber region from 100cm^{-1} to 2000cm^{-1} . The spectral resolution was several cm^{-1} . We also performed a line analysis in Raman scattering measurements.

3. Argon Excimer Laser and SiC Mirrors

With regard to a high power argon excimer laser which we have been developing, the detailed description about the electron beam machine for the pumping and the characteristics of the laser outputs have already been described elsewhere⁶⁾. We therefore briefly explain the laser set-up as illustrated in Fig.1, and describe the laser irradiation conditions of SiC films. The laser gas contained in an anode pipe was pumped by an electron beam. When an argon gas was used as the laser medium, the laser output was obtained at 126 nm ($h\nu = 9.8$ eV). The ends of the anode pipe opened into the high pressure chambers, where the optical elements of the laser cavity were placed. The output mirror used in these experiments was an uncoated MgF_2 plate. A SiC film was placed at the opposite end of the cavity as a reflector.

The output energy of the laser beam of 5 mm in diameter, which came out through the output

Fig.1 Schematic illustration of an electron beam pumped rare gas excimer laser.

Fig.2 SEM photographs from a SiC mirror surface of non-irradiated area (a) and irradiated area (b).

mirror and a pressure window of MgF_2 , was measured in vacuum. The highest values of the output energy per pulse and peak power so far obtained were 80 mJ in 5ns and 16 MW, respectively²⁾. The energy density on the sample surfaces was not directly measured and instead calculated from the laser output energy by taking account of the transmittance of the output mirror and window, 63 % each at 126 nm. The calculated value is $1\text{J}/\text{cm}^2$.

Fig.3 X-ray diffraction pattern of SiC film, showing that the film consists of polycrystallites with the 3C structure and that it has a preferred orientation in such a way that the surfaces are parallel to a (110) plane.

SiC films were prepared by a low-pressure CVD method at 1400°C on SiC substrates which were sintered and then pressed. The film thickness is about $170\text{ }\mu\text{m}$. They are light brown in color, which is different from black of the films previously used. The surfaces were lapped and then finished by a conventional optical polishing of the order of submicron. Figure 2(a) shows the SEM photograph of the SiC surface. There is no significant feature at the surface except the weak profile of the grain boundaries. The grain size is about $15\text{ }\mu\text{m}$, observed with an optical microscope after chemical etching of the surface.

An X-ray diffraction pattern of a SiC film, which was taken under a specular reflection condition with $\text{Cu K}\alpha$ radiation, is illustrated in Fig.3. It shows that the film mainly consists of SiC crystallites with a face-centered cubic structure (3C-SiC). Only a (220) peak at $2\theta = 60^\circ$ is strong, which indicates that the film has the preferred orientation in such a way that the film surface is parallel to a (110) crystallographic plane.

Figure 4 shows XPS spectra for Si 2p (a) and C 1s (b) core level emissions from a SiC film surface. Only one peak is seen in Fig.4(a),

Fig.4 XPS spectra of Si 2p (a) and C 1s (b) emission from the SiC mirror surface. H. C. represents hydrocarbon in the surface contaminants.

whose binding energy is 100.3 eV and full width at half maximum (FWHM) is 1.3 eV. The peak is attributed to the emission from the constituent silicon atoms in SiC. In Fig.4(b), the measured curve (solid line) is partitioned into two peaks (broken lines) at 282.5 and 285.1 eV. It is generally accepted in XPS studies that C 1s peak around 285 eV comes from hydrocarbon molecules which are adsorbed on the surface as contaminants. The peak at 282.5eV (FWHM is 1.1 eV) is then attributed to the emission from the constituent carbon atoms of SiC.

Figures 5(a) and 5(b) show Raman spectra in the wavenumber region from 100 cm^{-1} to 1100 cm^{-1} and from 1000 cm^{-1} to 2000 cm^{-1}

Fig.5 Raman spectra taken from the SiC mirror surface. Two sharp peaks in (a) are from SiC phonon modes, and some peaks in (b) from amorphous like carbon-carbon bonds.

respectively. In Fig.5(a), two sharp peaks locate at 797 and 976 cm^{-1} , which are attributed to a transverse optical (TO) and a longitudinal optical (LO) phonon mode of the 3C-SiC structure, respectively⁷⁾. The FWHMs are 4.7 (TO) and 5.7 cm^{-1} (LO). They are close to the value of 4 cm^{-1} for a single crystal⁸⁾, which indicates good quality of the SiC film. Shoulder peaks in the lower wavenumber side of the TO peak are probably due to the existence of other polytypes of SiC. A broad and weak peak around 530 cm^{-1} implies the existence of Si-Si bonds in SiC. In Fig.5(b), several broad peaks are observed with a prominent broad peak at 1524 cm^{-1} (45 cm^{-1} in FWHM) and a weak peak at 1405 cm^{-1} (40 cm^{-1} in FWHM). These peaks have been observed in graphite-like amorphous carbon with sp^2 configuration⁹⁾. This indicates that the films contain such amorphous carbon, which are

probably present in the grain boundaries. Other peaks at 1624 and 1715cm^{-1} cannot be well assigned, but they are possibly related to amorphous carbon because the FWHMs are comparable to that of the peak at 1524cm^{-1} . The origin of the peak at 1107cm^{-1} is unclear but this peak has no connection with the main subject. We will notice the peaks at 797 and 1524cm^{-1} later.

4. Damage Observations

When SiC films were irradiated with four pulses of $1\text{J}/\text{cm}^2$ per pulse of an argon excimer laser, surface roughening was clearly seen partly in the center on the samples with a naked eye. The diameter of the incident laser beam is 5mm . The SEM photograph of the roughened part shows ripples of many randomly distributed spots. The diameter of the spots is around $1.5\text{ }\mu\text{m}$. From the outskirt to the center of the roughened part, the spot density becomes the higher. Figure 2(b) shows the center of the roughened area. The surface is covered with the spots completely.

To investigate the change in the bonding nature with a microscopic scale which was induced by the laser irradiation, we measured XPS spectra of the roughened area. Figures 6(a) and 6(b) show the spectra of Si 2*p* and C 1*s* emission, respectively. Solid line indicates measured curve and broken lines indicate the peaks decomposed in the same way as in Fig. 4(b). From the comparison with Fig. 4(a), a prominent peak at 100.3eV (FWHM is 1.6eV) in Fig. 6(a) is assigned silicon atoms in SiC. In addition, the shoulder peak is also observed at 99.2eV (FWHM is 1.1eV). From the fact that the Si 2*p* signal from the crystal silicon is observed at the same binding energy, this shoulder peak is assigned to elemental silicon. It becomes clear that the silicon is precipitated in the surface layer of SiC films by the high energy laser

Fig. 6 XPS spectra of Si 2*p* (a) and C 1*s* (b) emission from a laser irradiated area, in which a shoulder peak at 99.2eV in (a) originates from elemental silicon. H. C. represents hydrocarbon in the surface contaminants.

irradiation. In Fig. 6(b), two peaks are observed at 284.5eV (FWHM: 2.1eV) and 282.7eV (FWHM: 0.9eV), which are assigned to hydrocarbon and SiC, respectively. The integrated intensity of SiC becomes less than a third of that in Fig. 4(b). This reduction in intensity suggests that the amount of SiC decreases in the surface layer by the silicon precipitation.

Figure 7(a) shows the Raman spectrum in the wavenumber region from 100 to 1100cm^{-1} . A broad peak is observed at 478cm^{-1} (73cm^{-1} in FWHM), in addition to the two sharp peaks which are also observed from the non-irradiated

Fig.7 Raman spectra from a laser irradiated area. A broad peak at 478cm^{-1} indicates elemental silicon in its amorphous state.

areas. For a peak identification, Raman spectra of a single crystal silicon (a) and an amorphous silicon (b) are presented in Fig.8. From the fact that a peak observed at 478cm^{-1} in Fig.7(a) is similar to the spectrum in Fig.8(b) rather than that in Fig.8(a), the precipitated silicon is concluded to be in an amorphous state. A high intensity region in the wavenumber below 200cm^{-1} is considered to be due to acoustic phonon modes from amorphous silicon, which is observed by Raman scattering because of the breaking of a selection rule. In Fig.7(b) is shown the Raman spectrum in the extended wavenumber region from 1000 to 2000cm^{-1} . The Raman intensity in Fig.7(b) is in the same scale as that in Fig.5(b). All peaks become weak, compared with those in Fig.5(b). No other noticeable change was observed in this region.

In order to investigate the spatial distribution

Fig.8 Raman spectra of crystal (a) and amorphous (b) silicon, together with the Raman spectrum from SiC irradiated with an ArF excimer laser (c).

of amorphous silicon, amorphous carbon, and crystalline SiC, we performed a line analysis of Raman scattering measurements for three peaks: amorphous silicon at 478cm^{-1} , amorphous carbon at 1524cm^{-1} , and TO phonon mode of SiC at 798cm^{-1} . The results are illustrated in Fig.9. At the center of the roughened part, the Raman scattering intensity of the amorphous silicon is higher than that in the out-skirt. The two others are lower in intensity at the center. The diameter of the silicon enriched area is about 2.5mm . The fact that the both peak intensities of the TO mode of SiC and of the amorphous carbon is weaker in the silicon enriched area, is an indication that carbon is depleted in this region.

Fig.9 Line analysis of Raman scattering. From the top to the bottom, peak intensities at 473 (amorphous silicon), 1520 (amorphous carbon) and 794cm^{-1} (TO mode of SiC) are shown as a function of position.

5. Discussion

5.1 Calculation of surface temperature

Sparks has discussed¹⁰⁾ laser heating of solids which is based on the heat conduction with various boundary conditions. Applying the theory to our case, we can calculate the maximum temperature at the surface of SiC film irradiated by the laser beam. The temperature rise is expressed by

$$T = 2IA (t/\pi CK)^{1/2} \quad (1)$$

where I is the irradiance (W/cm^2), A is the

absorptance, C is the heat capacity per unit volume ($\text{J}/\text{cm}^3\text{K}$), K is the thermal conductivity (W/cmK) and t is the irradiation time. The duration of the incident light is assumed to be larger than the time required for heat to flow down to the distance of the absorption depth and smaller than the time required for heat to flow down to the distance of the film thickness. For simplicity, C and K are assumed to be independent of a temperature. To calculate the maximum temperature, we substitute the pulse duration of 5ns for t . The other values needed in this calculation are listed in Table I¹¹⁾.

It is quite difficult to measure the irradiance of the SiC film surface experimentally. We assume the irradiance to be the value of the energy density on the SiC film surface divided by the pulse duration of 5ns. The energy density on the SiC film surface is estimated to be $1\text{J}/\text{cm}^2$ as is described in section 2. The calculated maximum temperature with the aid of equation (1) is 5940°C . This value is far above the sublimation or decomposition temperature about 2700°C ¹²⁾. From the result of the temperature calculation of SiC film surface, the surface layer of SiC might have melted and decomposed during the laser irradiation. It is consistent with the surface topographical roughening observed by SEM. The damage generating threshold of the SiC mirror can be estimated by this calculation of the temperature rise at the surface to be $450\text{mJ}/\text{cm}^2$.*)

5.2 Radiation effects

As is discussed in the previous subsection, the laser irradiation leads SiC surface temperature above the decomposition temperature and pos-

*) The threshold value estimated here is different from that reported in Ref.11. The equation (1) includes the effect of temperature distribution of the mirror, while this effect is neglected in Ref.11.

Table I The parameters used in the calculation of the temperature rise according to Ref.10¹¹⁾.

Physical quantity	: Value
absorption length	: $\alpha = 4.66 \times 10^{-7} \text{ cm}$
sample thickness	: $l = 170 \mu\text{m}^{\text{a)}$
laser-beam diameter	: $D = 5 \text{ mm}$
heat capacity per unit volume	: $C = 2.144 \text{ J cm}^{-3} \text{ K}^{-1\text{b)}$
thermal conductivity	: $K = 0.9 \text{ W cm}^{-1} \text{ K}^{-1}$
laser pulse width	: $t = 5 \text{ ns}$
absorptance	: $A = 0.517$
irradiance	: $I = 200 \text{ MW cm}^{-2 \text{ b)}$

a) Measured value.

b) Estimated values from the data in ref.11.

Fig. 10 Reflectivity (solid line) and absorption coefficient (broken line) of SiC as a function of wavelength.

sibly causes a thermal decomposition of SiC. The absorption coefficient and reflectivity of SiC are plotted as a function of wavelength in Fig.10. They are calculated based on the refractive indices in ref. 13. SiC has relatively high reflectivity from 30 to 50%, which is a desirable property for laser mirrors, in the wavelength range from 40 to 250nm. In this range the absorption coefficient is larger than 10^5 cm^{-1} . When SiC mirrors are exposed to high power lasers whose wavelength is in this range, such thermal decomposition might occur as a result of an absorption of the intense laser light. In

fact, radiation damage has been also found in the surface layer after a SiC mirror was exposed in air to 5 pulses of 3 J/cm^3 per pulse from an ArF excimer laser whose wavelength and pulse duration are 193nm and 20ns respectively. These findings imply that SiC is decomposed thermally. As seen in the Raman spectrum of Fig. 8(c), crystalline silicon is detected as well as amorphous silicon in case of ArF excimer laser exposure. The successive laser irradiation is considered to induce the crystallization.

The vapor pressure of elemental silicon is the order of 10^3 Torr at 2700°C where that of elemental carbon is around 10^{-3} Torr at the same temperature¹⁴⁾. From this point of view, silicon atoms escape more preferably from the surface and elemental carbon should precipitate rather than elemental silicon. Therefore we cannot simply conclude that the surface temperature rise leads silicon precipitation and carbon depletion.

P. V. Huong et al.¹⁵⁾ observed a Raman peak at 522 cm^{-1} , corresponding to crystalline silicon, when SiC films were irradiated with an argon ion laser at 514.5nm with a power of 7W. They concluded that SiC was decomposed by laser in-

duced chemical reaction with oxygen, namely that carbon was removed as carbon dioxide. As a result, silicon is precipitated in the surface layer and then crystallized by a laser annealing effect. It should be emphasized in their results that no decomposition of SiC was observed without oxygen atmosphere. Their results show that oxygen atmosphere plays an important role to remove carbon from SiC film surface. On the other hand, SiC was irradiated in Ar atmosphere in our experiment and we found the damages in the mirrors. Our results are not consistent with the results reported by Huong et al. To explain laser induced damages in the VUV region within the framework of their interpretation, we consider that oxygen assists to remove carbon atoms selectively by forming CO₂ or CO. Oxygen is probably present on the SiC mirror surfaces.

We speculate the mechanism of SiC mirror damage occurrence as follows: SiC absorbs the intense VUV laser light, the temperature rises over the decomposition temperature¹²⁾ and hence the SiC undergoes a thermal decomposition. Constituent carbon atoms are removed from the SiC surface in terms of a chemical reaction with oxygen adsorbed on the surface and then silicon atoms remain at the surface to form amorphous silicon.

The radiation effects of an argon excimer laser on the SiC mirrors used in the present experiments are found to be similar to those on SiC mirrors reported before³⁾. We speculate that the radiation effects do not depend on whether the materials is crystalline or not.

6. Conclusions

Polycrystalline SiC films were deposited on sintered and then pressed SiC substrates by a low-pressure CVD method and the radiation effects of high energy laser irradiation on the

film were investigated. From a surface temperature estimation and SEM photographs, we conclude that the surface of SiC film was heated up to a temperature exceeding by far the melting point. On the bases of the Raman scattering and XPS spectra, elemental silicon is found to be formed in its amorphous state at the surface. The present result is similar to that observed for SiC mirrors consisting of fine particle, and thus silicon precipitation due to high power VUV laser irradiation is considered to be an inherent feature for SiC mirrors.

SiC was considered to be a good candidate for reflective mirrors for high-power lasers and synchrotron radiation, in particular for radiation in the spectral range from vacuum to extreme ultraviolet. However we found that the laser radiation as high as 1J/cm² induced the surface transformation into amorphous silicon as well as the surface roughening. Since large values of absorption coefficient turn out high values of reflectivity, surface temperature rise could not be avoided when the property of high reflectivity is utilized. Materials other than SiC should be developed for reflective mirrors of high power radiation with wavelength in which almost all materials show large absorptance. The material with a high thermal conductivity and a high melting temperature such as a diamond is applicable to the reflective mirrors of the VUV lasers.

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