Chemical-Bonding-State Analysis of Silicon Carbide Layers in Mo/SiC/Si Multilayer Mirrors Using Soft X-Ray Spectroscopy

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INTRODUCTION

Functional multilayer mirrors, such as highly heat-resistant multilayer mirrors, have been strongly required for the future highly brilliant synchrotron radiation beamlines and high-flux x-ray optical systems. As highly heat-resistant multilayer mirrors, various multilayer mirrors with interleaved barrier-layers made of compounds, rather than single elements, to suppress interdiffusion have been developed; for example, Mo/SiC/Si [1]. The reflectivity and heat-resistivity of such multilayer mirrors strongly depend on the chemical-bonding-states of the compound barrier-layers and their interlayers. Chemical-bonding-state analysis of the inner compound-layers is therefore important for the development of functional multilayer mirrors.

Our goal in this study is to analyze the chemical-bonding-states of the inner layers, which consist of compounds, in multilayer mirrors by using soft x-ray emission and absorption (SXEA) spectroscopy. In this paper, we describe the high-resolution C K x-ray emission and absorption spectra of the Mo/SiC/Si multilayer mirrors, and discuss the chemical-bonding-states of the silicon carbide layers revealed by molecular orbital calculations.

EXPERIMENT

Mo/SiC/Si multilayer mirrors were prepared by r.f. magnetron sputtering methods [1]. 7-Å-thick SiC layers were deposited between 26-Å Mo and 27-Å Si layers. Forty periods of the SiC/Si/SiC/Mo layer-structure were accumulated on a silicon wafer. Spectroscopic measurements of x-ray emission and absorption in the C K region were made at the Advanced Light Source (ALS). X-ray emission spectra were measured using a grating x-ray spectrometer installed in beamline (BL) 8.0 [2]. The resolving power (E/ΔE) of the spectrometer was estimated to be higher than 500 in the C K region, using a 50-μm entrance slit and a 600-lines/mm spherical grating which had a 10-m radius. The total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2 [3]. The resolving power of the TEY absorption measurements was estimated to be about 1600 using a 600-lines/mm variable-line-spacing grating and a 20-μm exit slit.

RESULTS AND DISCUSSION

Figure 1 shows (a) x-ray emission and (b) TEY absorption spectra in the C K region of the as-deposited and 600˚C annealed Mo/SiC/Si multilayer mirrors. Spectra of hexagonal (*h*) SiC, cubic (*c*) SiC, graphite, amorphous carbon, and diamond are also shown in the figure for reference. In the emission spectra (a), peak widths of both the as-deposited and annealed multilayers are narrower than those of graphite, amorphous carbon, and diamond. Spectral features of the multilayers are also clearly different from those of the reference carbon materials. Although the peak widths of the multilayers are similar to those of *h*- and *c*-SiCs, the symmetric peak shape of the multilayers differs from the low-energy-tailed peak shape of the reference SiCs. This indicates that carbon atoms in the multilayers may form Si-C bonds, but these chemical states in the multilayers are different from those of the reference *h*- and *c*-SiCs. In the absorption spectra (b), both the multilayers show the three-peaked features, which clearly differ from the spectral features of the graphite, amorphous carbon, and diamond. Although the reference *h*- and *c*-SiCs also show the three-peaked features, their relative peak intensities among the three peaks are slightly different from those of the multilayers. This also implies that the carbon atoms in the multilayers form Si-C bonds, but their chemical states differ from those of the reference SiCs.

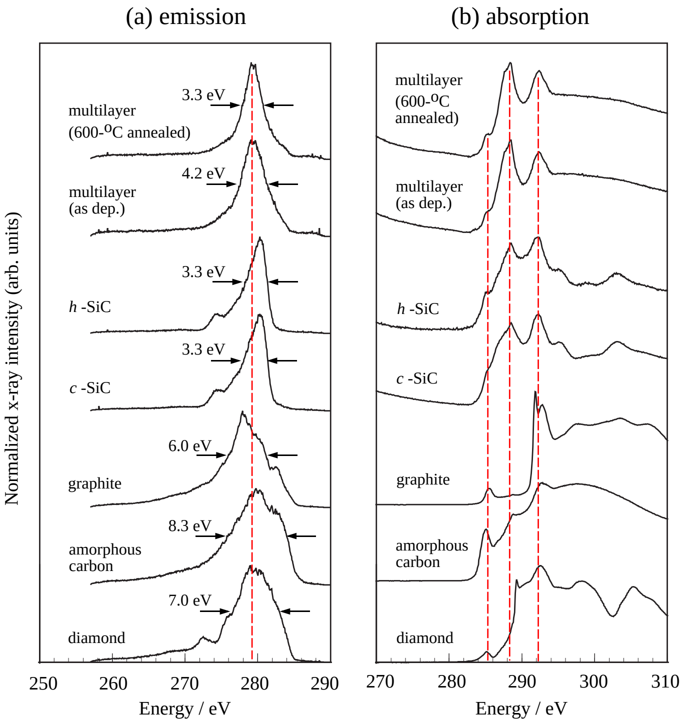

Figure 1 C K x-ray emission (left) and absorption (right) spectra of the as-deposited and 600°C annealed multilayers. Spectra of the *h*-SiC, *c*-SiC, graphite, amorphous carbon, and diamond are also shown for reference.

To analyze the chemical states of the carbon atoms in the silicon carbide layers in the multilayers, we calculated the C2p density of states (DOS) of several silicon carbide models, and compared their calculated DOS spectra with the measured x-ray spectra. Figure 2 shows the silicon carbide model clusters based on (a) *c*-SiC and (b) *h*-SiC. In the *c*-SiC-based models (a), a type I model ($Si_{10}C_4H_{24}$) represents the standard *c*-SiC structure. In the type II model ($Si_9C_5H_{24}$), one silicon atom (labeled no. 5 in the type I model) was replaced by a carbon atom, which resulted in a carbon-excessive *c*-SiCx structure. In the *h*-SiC based models (b), a type I model ($Si_{10}C_{10}H_{38}$) represents the standard *h*-SiC structure. Type II and III models ($Si_9C_{11}H_{38}$) are obtained by replacing silicon atoms nos. 14 and 11 in the type I model by carbon atoms; this also resulted in a carbon-excessive *h*-SiCx structure.

Figure 3 shows the occupied C2p and C2s-DOS spectra of the above-mentioned silicon carbide models, with the corresponding measured x-ray emission spectra of *c*-SiC, *h*-SiC, and the annealed multilayers superimposed. Each spectrum was obtained by broadening the individual DOS with 0.5-eV-wide Lorentzian functions. For the *c*-SiC- and *h*-SiC-based type I models, their C2p-DOS spectra are in good agreement with the measured x-ray emission spectra of *c*- and *h*-SiC, respectively. This may show that the C2p-DOS spectra can adequately reproduce the measured CK x-ray emission spectra. For the *c*-SiC-based type II and *h*-SiC-based type III models, the low-energy tails in their C2p-DOS spectra were rather reduced compared with those of the standard *c*- and *h*-SiC models. Consequently, the measured CK x-ray emission spectra of the multilayers can be approximately reproduced by these carbon-excessive models. Unoccupied C2p-DOS spectra of the carbon-excessive models were also similar to the x-ray absorption spectra of the multilayers. We therefore conclude that the chemical states of the silicon carbide layers in the Mo/SiC/Si multilayers are probably carbon-excessive silicon carbide.

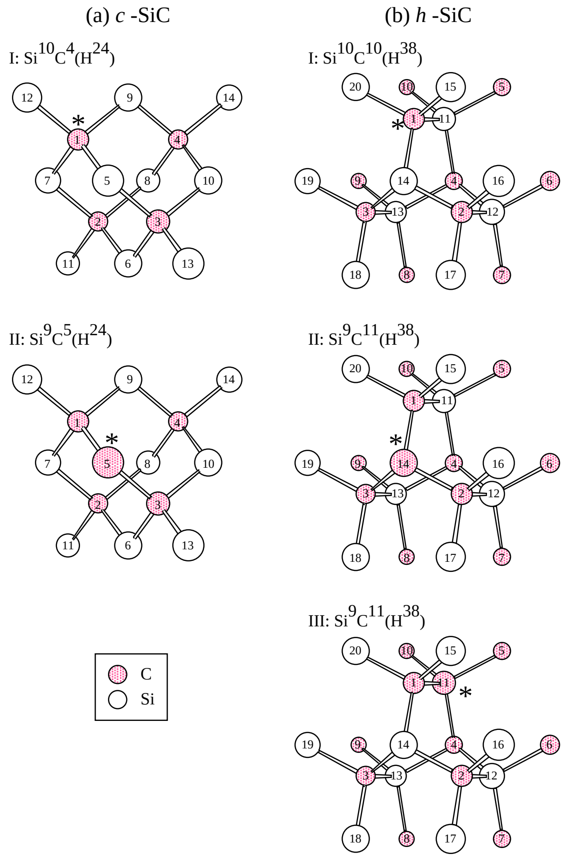

Figure 2 Model clusters for the silicon carbide layers, based on (a) *c*-SiC and (b) *h*-SiC. Type I models represent the standard *c*- and *h*-SiC. Types II and III represent the carbon-excessive models. Carbon atoms from which the DOS spectra were obtained are denoted by asterisks.

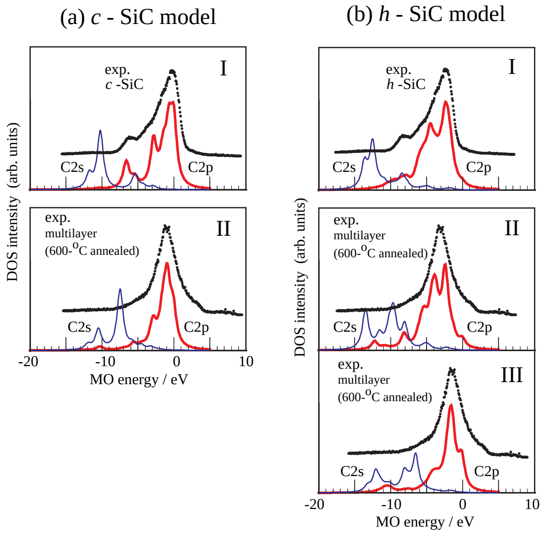

Figure 3 Occupied and unoccupied C2p- and C2s-DOS spectra of the silicon carbide models. Measured C K x-ray emission spectra of *h*- and *c*-SiC are superimposed on the corresponding type I models, and those of the annealed multilayer on the type II and III models.

ACKNOWLEDGMENTS

We thank Dr. Takayoshi Hayashi of NTT Lifestyle and Environmental Technology Laboratories for useful discussions. We are also grateful to Professor Thomas A. Callcott of the University of Tennessee for his helpful support in the spectroscopic measurements at BL-8.0. This work was supported by NTT.

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