ESR Measurements of HOPG Irradiated with Highly Charged Ions*

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Electron spin resonance (ESR) measurements were performed on highly oriented pyrolytic graphite (HOPG) samples irradiated with highly charged ions (HCIs). The interaction between a HCI and surfaces results in emission of photons in the range of visible to X-ray, hundreds of secondary electrons, sputtering of secondary ions and modification of surface structure in nanometer scale. In the present experiments, HCIs were produced by electron beam ion source (EBIS) and Ar\(^{14+}\) and Ar\(^{11+}\) were used for the irradiation. ESR measurement provides information on unpaired electrons of the sample. We investigated the persistence of defect formation on charge state and fluence of incident HCIs using ESR. The L1 line appeared in HOPG samples irradiated with HCIs at the low temperature region, and the intensity became larger at higher charge state and higher fluence. [DOI: 10.1380/ejssnt.2018.356]

Keywords: Highly charged ion; HOPG; Electron spin resonance; Ion bombardment; Ion implantation; Ion-solid interactions

I. INTRODUCTION

The highly charged ion (HCI) has large potential energy increasing with its charge state. For example, Ar\(^{14+}\) has a potential energy of about 4 keV and U\(^{92+}\) has that of about 800 keV. The interaction between a HCI and surfaces results in emission of photons in the range of visible to X-ray, hundreds of secondary electrons, sputtering of secondary ions and modification of surface structure in nanometer scale. The effect of the kinetic energy on the material extends to a deep region, while the potential energy concentrates on only a few atomic layers of the topmost surface [1, 2]. HCIs have large potential energy and can cause a significant interaction with the surface regardless of their kinetic energy. Therefore, it is possible to minimize the influence of irradiation on subsurface layers by using slow HCIs. Surfaces irradiated with HCI has been analyzed using scanning tunneling microscope (STM), atomic force microscope (AFM), scanning electron microscope (SEM) and Raman spectroscopy [3–5].

Highly oriented pyrolytic graphite (HOPG) samples irradiated with monovalent ions have been studied by electron spin resonance (ESR) and superconducting quantum interferometer device (SQUID) as a study of magnetism of HOPG irradiated with ions [6–9]. When a proton was injected, resonance peak due to the ion injection was observed at the fluence of 10\(^{16}\) cm\(^{-2}\). ESR measurements of HOPG irradiated with Ar\(^{11+}\) were performed in the previous study and two lines were observed in the ESR spectra at the low temperature region, however, little is known about the dependence of ESR spectra on charge state and fluence [10].

In the present study, HOPG samples irradiated with Ar\(^{q+}\) were measured by ESR in order to investigate the dependence of defect formation at the surfaces on charge state and fluence.

II. EXPERIMENTAL

The experiments were performed using the electron beam ion source (EBIS) installed at Kobe University, Japan. Figure 1 shows a conceptual diagram of the Kobe EBIS [11, 12]. The Kobe EBIS consists of an electron gun, drift tubes, an electron collector and a superconducting magnet. Electron beam with the current in the order of 100 mA is focused by the strong magnetic field (3T) generated by a superconducting magnet. The current density at drift tube region is in the order of 1000 A/cm\(^2\). HCIs are created by successive ionization processes in the collision of electrons with an ion. The potential of drift tube, i.e., acceleration voltage to HCIs, is 3 kV. The ultimate pressure of the Kobe EBIS is about 10\(^{-8}\) Pa. Figure 2 shows whole experimental setup of the present experiment. The charge state of HCIs extracted from the ion source is selected by using a sector magnet. The extracted HCIs enter the irradiation chamber maintained at ultrahigh vacuum of about 10\(^{-7}\) Pa. Primary ion current is monitored by a Faraday cup and the ion beam shape is

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FIG. 1. Conceptual diagram of Kobe EBIS.
monitored by a micro-channel plate (MCP), and incident ion current to the sample during irradiation is also monitored.

In the present experiments, HOPG samples were irradiated with Ar\(^{8+}\) and Ar\(^{14+}\). The fluence of Ar\(^{8+}\) per hour was about \(6 \times 10^{13}\) ions/cm\(^2\) and that of Ar\(^{14+}\) was about \(7 \times 10^{12}\) ions/cm\(^2\). When the charge state of HCIs is different, the kinetic energy of HCIs differs at same acceleration voltage. To avoid this, different deceleration voltages were applied to the sample for each charge state in order to unify the kinetic energy (16 keV). This makes it possible to purely evaluate the effect of the potential energy of HCIs. After irradiation, the HOPG samples were measured by an X-band ESR apparatus (BRUKER, EMX8/2.7). The sample extracted from the irradiation chamber to atmosphere was vacuum sealed in a quartz tube and cooled by liquid helium and its temperature was controlled by heater and flux of liquid helium. In these experiments, the samples were analyzed with the direction of microwave perpendicular to the \(c\) axis.

III. RESULTS AND DISCUSSION

Figure 3 shows the ESR spectra of the HOPG irradiated with Ar\(^{14+}\) at a fluence of \(1 \times 10^{14}\) ions/cm\(^2\). These spectra were obtained at temperatures ranging from 10 K to 260 K. There are two resonance lines in the spectra at low temperatures. A Dysonian line (D1 line) was observed in lower resonance field. A Lorentzian line (L1 line) appeared at low temperatures in higher resonance field. The L1 line decreases with increasing temperature and this line was not observed in measurement of unirradiated HOPG sample [10]. Because unpaired electrons result in ESR signal, it is considered that the L1 line is originated from defects (dangling bonds) formed by Ar\(^{14+}\) irradiation.

Figure 4 shows ESR spectra and Fig. 5 shows L1 line intensity observed in ESR spectra for four irradiation conditions at 10 K. The L1 line intensity for Ar\(^{14+}\) is larger than that for Ar\(^{8+}\) at the fluence of \(1 \times 10^{14}\) ions/cm\(^2\). It is supposed that the difference in L1 line intensity of Ar\(^{8+}\) and Ar\(^{14+}\) was caused by that of potential energy of HCIs because the irradiation was performed with constant kinetic energy for different charge states. The L1 line of Ar\(^{14+}\) is about twice that of Ar\(^{8+}\) and it is suggested that the contribution of the potential energy is dominant over the kinetic energy for defect formation by irradiation of HCIs. Most of the potential energy of HCIs is dissipated at only some layers of topmost surface and forms irrad-
FIG. 4. ESR spectra of the HOPG samples irradiated with Ar\(^{8+}\) at the fluence of \(1 \times 10^{14}\) ions/cm\(^2\) and \(3 \times 10^{14}\) ions/cm\(^2\), with Ar\(^{14+}\) at the fluence of \(3 \times 10^{14}\) ions/cm\(^2\) and \(1 \times 10^{14}\) ions/cm\(^2\) at 10 K.

FIG. 5. L1 line intensity observed at ESR spectra of HOPG irradiated with HCIs (Ar\(^{8+}\) and Ar\(^{14+}\)) at 10 K as a function of the fluence of HCIs.

ation traces on the HOPG surface [2, 13]. Since a single HCI injected in a HOPG surface makes one dot structure with 100% probability [14], it is considered that dangling bonds are produced by the potential energy of HCIs on the sample surface with high efficiency.

Comparing ESR spectra of HOPG samples irradiated with HCIs, L1 line intensities of Ar\(^{8+}\) and Ar\(^{14+}\) increase depending on the fluence. For the case of Ar\(^{8+}\), the L1 line intensity of \(1 \times 10^{14}\) ions/cm\(^2\) is about three times that of \(3 \times 10^{14}\) ions/cm\(^2\). Based on these results, it is considered that the dangling bonds increase almost linearly with the fluence of HCIs.

From the present experiment and the previous study [10], it is supposed that magnetic modification by HCIs appears in smaller fluence than by monovalent ions. Actually, SQUID measurements indicate that HOPG samples irradiated with Ar\(^{14+}\) at the fluence in the order of \(10^{14}\) ions/cm\(^2\) have greater magnetizations than samples irradiated with monovalent ions at the fluence of \(1.875 \times 10^{15}\) ions/cm\(^2\) as in Ref. [9].

It is necessary to perform measurements over various charge state and fluence in order to reveal the effect of potential energy on magnetic modification of materials by HCI injection in detail.

By virtue of the high efficiency in magnetic modification and controllability of defect size using HCI injection while minimizing the contribution of kinetic energy, the single ion implantation of a HCI could be applied to microfabrication for spintronics applications.

IV. CONCLUSIONS

In conclusion, we observed ESR spectra of HOPG samples irradiated with HCIs. There are two resonance lines, D1 line and L1 line in the spectra at low temperatures. The L1 line was not observed in unirradiated HOPG sample. This line is considered to be caused by dangling bonds produced by irradiation with HCIs. The L1 line intensity of Ar\(^{14+}\) is larger than that of Ar\(^{8+}\) at the same fluence of \(1 \times 10^{14}\) ions/cm\(^2\). This is because of the effect of the potential energy of HCIs. The L1 line intensity increases almost proportional to the fluence. Therefore, it is suggested that the defects of HOPG is roughly proportional to the fluence of HCIs.

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