Surface modifications of sapphire, diamond, and Ni-based alloys

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Co implanted sapphire emits brilliant sky-blue color and H^+ ions implanted diamond shows a purple-red color both after post-implantation annealing. The ion beam mixing results in highly sustainable SiC film deposited on Ni-based alloys at 1000°C in air. The proposed work has not been finished yet.

キーワード：Ion implantation, optical property, surface analysis, ion beam mixing

1. 目的

In order to modify the optical properties of sapphire and diamond materials, a method of the ion-implantation and subsequent annealing was used. The application areas include the coloration of diamond and sapphire when used as gemstones and optoelectronic applications as thin films. To understand the change in optical properties, calculation of the band structure using density functional theory (DFT) and characterizations of surface chemical properties before and after the ion implantation and subsequent annealing are employed.

Ion beam mixing[1-3)] of a thin SiC film deposited onto Ni-based alloys such as Hastelloy X and Haynes HX was conducted to enhance the adhesion, aiming at increasing the corrosion resistance of this materials in sulfuric acid and SO_2/SO_3 vapor environment at the temperature range of 600°C -950°C for the nuclear hydrogen production [4)].

２．方法

100 keV Co and B ions using 400keV ion accelerator and 1MeV H ions using 3MV Tandem accelerator were implanted into the sapphire and diamond samples with a dose of about 10^{17} ions /cm^2 for all samples. Post-irradiation annealing at 600°C– 1200°C were conducted both in air and in vacuum atmosphere for 2-24 hours. Once a certain changes in the optical properties of the treated diamond and sapphire specimens were visually observed, the relevant samples were analyzed with XPS, ED-XRF, and FTIR to understand the mechanisms of the changes. In order to examine the band gap variation in the doped diamond and sapphire, calculations by first-principles density-functional theory (DFT)[5)] were done.

About 100nm thick SiC coating on Ni-based alloys such as Hastelloy X and Haynes HX were conducted, and then 150 keV N ions were implanted in order to obtain a highly adherent coating layer onto the substrates. Since the materials developed in this study will be used in SO2/SO3 environment at the temperature above 900°C, the resistance against the corrosion and the endurance against the thermal stresses are examined and then such property changes will be correlated to the interfacial properties of the SiC film/ substrate as analyzed with AES elemental mapping and AES line-scan techniques across the interface.

３．研究成果

Fig. 1 is a photo of purple-red diamond produced by proton (H^+ ion) implantation and subsequent annealing at 600°C in vacuum for 2 hours. As shown in Fig. 2, Fe, Cr and Co implanted originally transparent sapphire shows, respectively, yellow, light yellow and sky-blue colors after post-implantation annealing at 900°C in air for 6 hours. The yellow and light yellow color emissions produced by Fe and Cr ions implantation were obtained from the previous experiment (Fig. 2a and -b). Annealing at 1150°C reduces the intensity of color, but the color seem to be propagated more deeply inside. Up to now, the other samples showed nothing but black even after annealing.

X-ray photo-electron spectroscopy (XPS) analysis was conducted on the Co implanted sapphire which showed the sky-blue color. Fig. 3 shows Co2p XPS peaks obtained from as-implanted (Fig. 3a) and post-implantation annealed (Fig. 3b) sapphire samples. Co2p peak at 778.7eV[6)] which denotes metallic Co is clearly seen along with Co-Al-O peak at 782.2eV[6)] in the as-implanted sapphire (Fig. 3a) while the peak corresponding to metallic Co disappeared in the post-implantation annealed sample (Fig. 3b). Electron dispersive X-ray fluorescent spectroscopy (ED-XRF) of yellow colored sapphire shows the existence of Fe as well as other trace elements such as Ga, Cr, etc (Fig. 4). Fig. 5 is FTIR spectra for the sky-blue colored sapphire implanted with Co ions followed by annealing. The broad absorption band in the range of 588nm to 626nm wavelength seems to be affected by Co ion implantation. On the other hand, the absorption peaks at around 388 and 450nm wavelength seem to be associated with Fe^{3+} that may have inherently existed in the sapphire before the ion beam bombardment.

Fig. 6a shows the band structure of N-doped diamond. The band gap of N-doped diamond can be estimated to be 3.01eV which is reduced by 1.12 eV as compared to the band gap (4.13eV) of the clean diamond. The experimental band gap of diamond is about 5.5eV. Such a large underestimation (~ 25%) of the band gap is the well-known shortcoming of the LDA. Fig. 6b is the band structure of H-doped diamond. The band gap of H-doped diamond can be estimated to be 2.17eV which is reduced by 1.96 eV as compared to that of the clean diamond.

150 keV N ion bombarded thin SiC film deposited on Hastelly X sustained after heating at 1000°C while the SiC film in non-implanted sample was completely peeled-off after annealing at 950°C. The corrosion test has not been conducted yet.

４．結論・考察

In our previous study, the N-ion-implanted diamond showed only black even after post-implantation annealing. In this study, noticeably, the purple-red color was emitted from the diamond as a result of an implantation with proton (H^+ ion) and subsequent annealing at 600°C in vacuum for 2 hours (Fig. 1). The color emission is due to selective reflection or transmittance of the visible light, which is caused by the existence of defects, lattice distortion, or impurity atoms. The defect and lattice distortion in diamond may have existed inherently and/or produced by the ion implantation, and they should be reduced by the heat treatment. Since the reduction of impurity atoms by out-diffusion during annealing is less likelihood in the ion implanted sample, the change in optical property due to the impurity atoms is more permanent. Since the DFT calculation shows a significant difference in the band gap between N and H doped diamonds, we conclude the different elemental doping plays a major role in the optical property change. This becomes clearer in the doped sapphire as shown in Fig. 2; that is, the originally transparent sapphire emitted all different colors when implanted with Fe, Cr and Co. However, different elemental doping not always seems to produce different colors as the implantation with Fe and Cr produced a similar color but the different saturation at the same ion dose.

The yellow and light yellow color emissions produced by Fe and Cr ion implantation (Fig. 2a and -b) were obtained from the previous experiment in which the post-implantation annealing was conducted in air at 900°C. Annealing at 1150°C makes the color lighter, but the color seem to be propagated into the deeper inside. In this work, Co implanted sapphire emitted sky-blue color after post-implantation annealing at above 900°C in air. This color is not normally found in the as-received sapphire. It is also noticeable that all the as-implanted samples showed a black color which seems to be associated with the defects formed by an ion bombardment, because the defects act as light absorption centers. As shown by X-ray photo-electron spectroscopy (XPS) analysis on the Co implanted sapphire, a large part of Co atoms in as-implanted sapphire exists as metallic Co whereas most of them convert to Al-Co-O compounds after the heat treatment. Therefore, it can be concluded that the formation of this compound is responsible for the sky-blue color emission. As analyzed with ED-XRF the trace elements such as Ga, Cr, etc exist in the sapphire (Fig. 4). Such trace elements do not seem to influence the optical band gap, because the sapphire was originally transparent, implying that the concentration of these trace element is not so sufficient to change the optical property. The broad absorption band in the range of 588nm to 626nm wavelength seemingly affected by Co ion implantation and the absorption peaks at around 388 and 450nm wavelength are believed to be responsible for the sky blue color emission, because the remaining wavelength range seemingly corresponds to the blue color.

The high sustainability of the SiC film deposited on Hastelloy X during heating at 1000°C is attributed to the mixed interface due to the 150 keV N ion bombardment. However, the energy of ions should be decided by the initial SiC film thickness, because the ion range at the film/substrate interface is a function of the bombarding energy and the film thickness; that is, in general, hicker film requires higher energy.

In summary, the optical properties of diamond and sapphire can be modified with ion implantation and subsequent annealing. Such modification is due to the band structural change due to the atomic substitution and the chemical reaction. Ion beam mixing is working well for the adhesion enhancement of SiC film deposited onto the Ni-based alloys.

The post-implantation annealing and characterization of the samples are still progressing. It will take a few months more to obtain more concrete and detailed results regarding this work.

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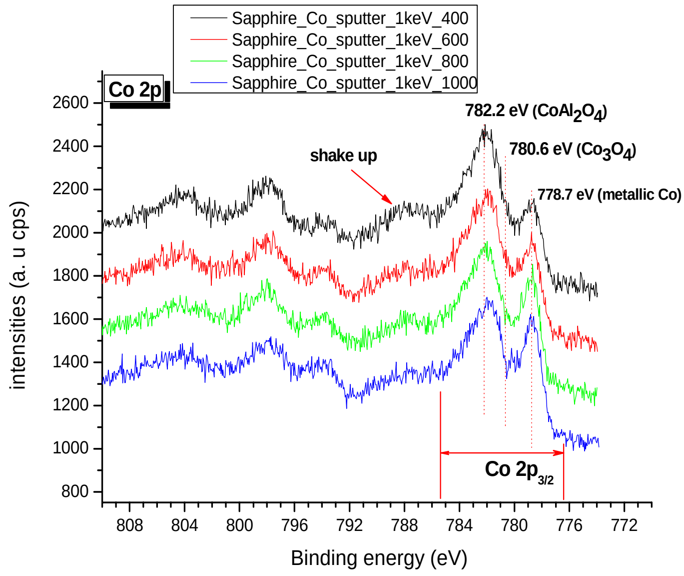
Fig. 1 Photo of purple-red diamond produced by proton (H^+ ion) implantation and subsequent annealing at 600℃ in vacuum for 2 hours.

(a)

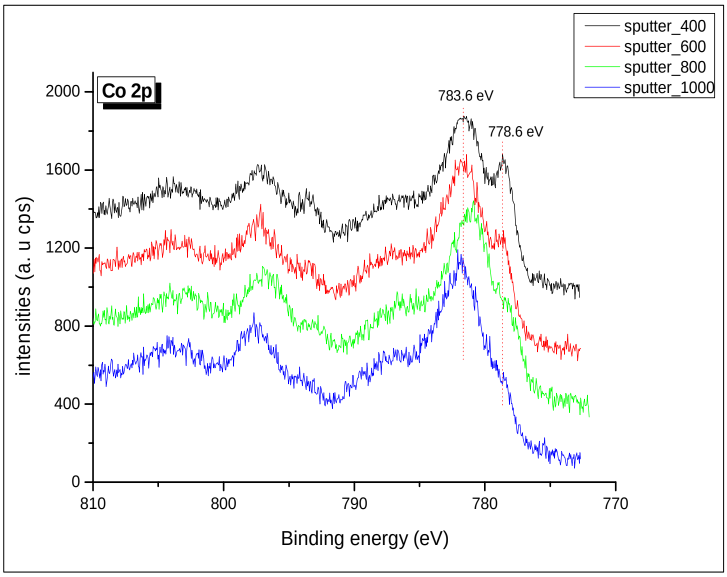
(b)

(c)

Fig. 2　Fe, Cr and Co implanted originally transparent sapphire shows, respectively, yellow(a), light yellow(b) and sky-blue (c) colors after post-implanted annealing at 900°C in air for 6 hours.



(a)



(b)

Fig. 3 Co2p XPS peaks obtained from as-implanted (a) and post-implantation annealed (b) sapphire samples. Co2p peak at 778.7eV which denotes metallic Co is clearly seen along with Co-Al-O peak at 782.2eV in the as-implanted sapphire (a) while the peak corresponding to metallic Co disappeared in the post-implantation annealed sample (b).

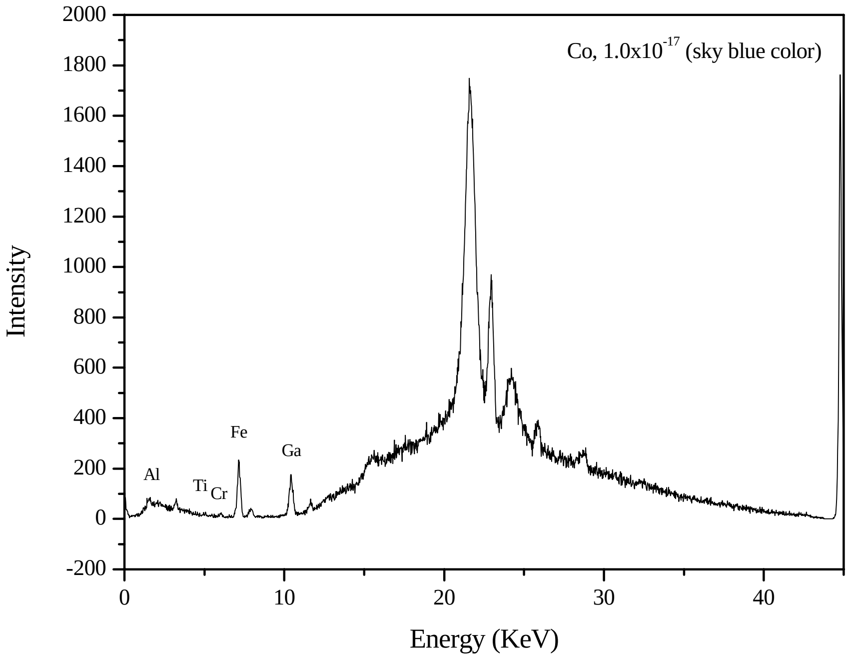


Fig. 4 Electron dispersive X-ray fluorescent spectroscopy (ED-XRF) of yellow colored sapphire shows the existence of Fe as well as other trace elements such as Ga, Cr, etc.

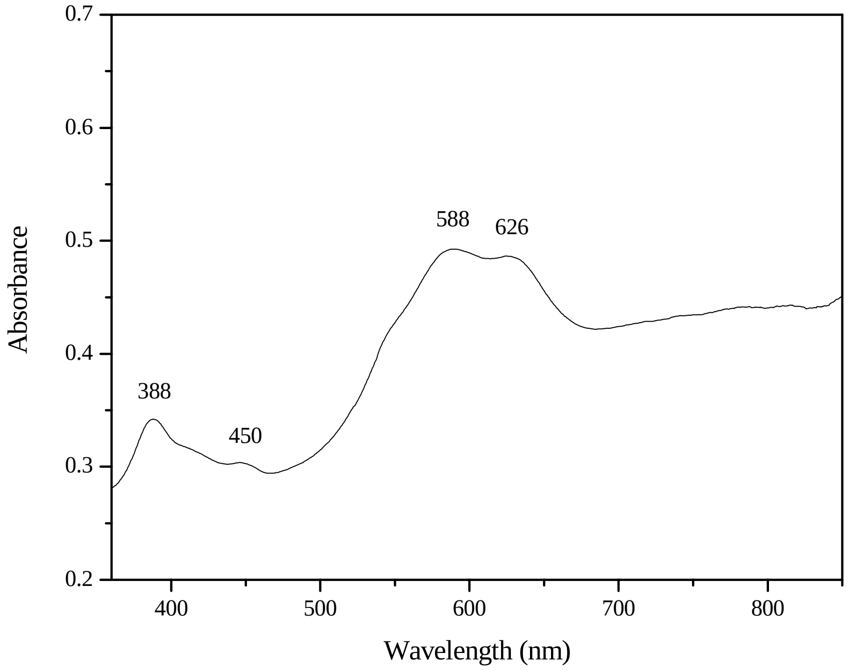


Fig. 5 FTIR spectra for the sky-blue colored sapphire implanted with Co ions followed by annealing. The broad absorption band in the range of 588nm to 626nm wavelength seems to be affected by Co ion implantation.

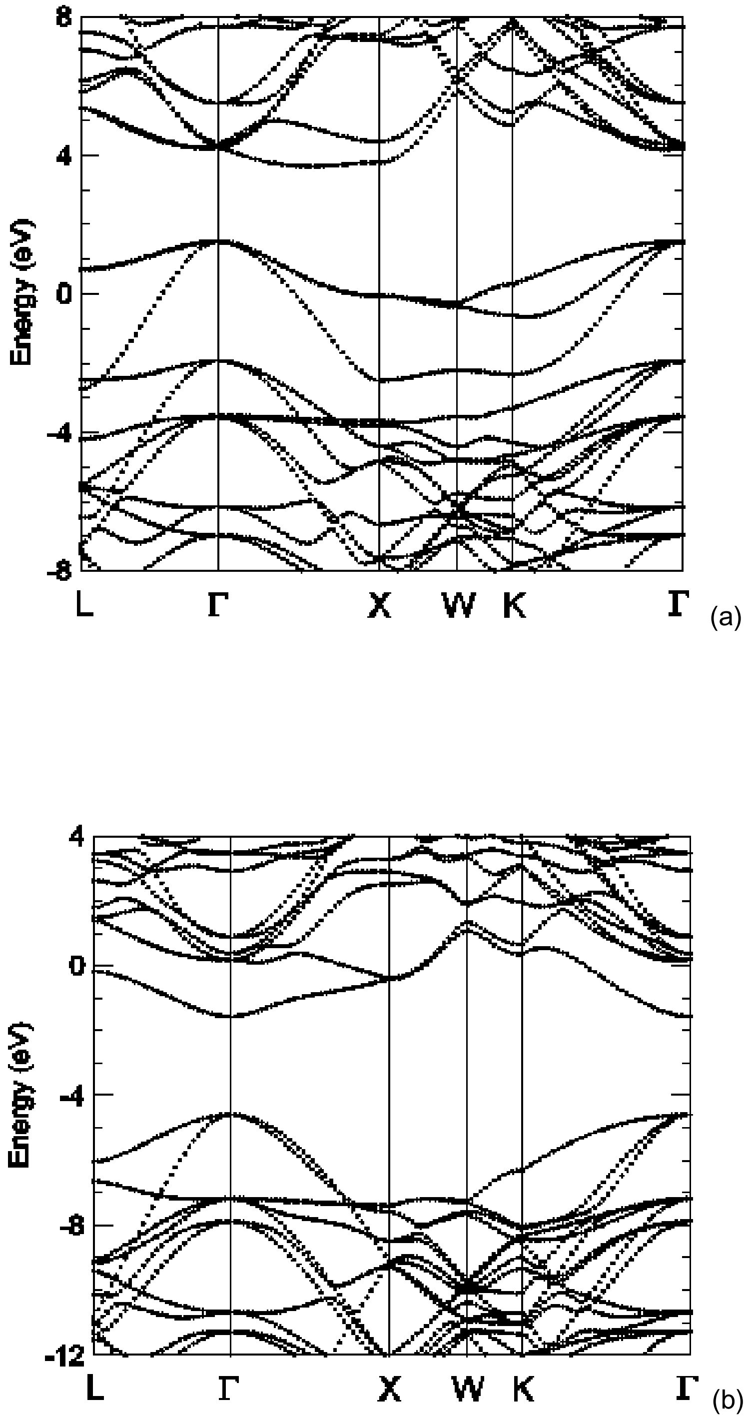


Fig. 6 The band gap of N-doped diamond can be estimated to be 3.01eV which is reduced by 1.12 eV as compared to the band gap (4.13eV) of the clean diamond (a) while the band gap of H-doped diamond can be estimated to be 2.17eV which is reduced by 1.96 eV (b).