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

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(要約2～3行)

The density of green color of diamond produced by proton irradiation is dependent on its inherent color. Mg ion implantation into colorless sapphire turned the sapphire brown, and the brown color disappears after annealing in the air, recovering the transparency.

The cross section energy dispersive spectroscopic analyses of N ion implanted SiC(2000Å)/Maxthal(2000Å)/Hastelloy X substrate specimen revealed the presence and accumulation of nitrogen ions in Maxthal side and of Al atoms recoil-implanted from Maxthal film in Hastelloy X side, implying that the ion beam mixing occurred.

キーワード: Proton irradiation, Ion implantation, Optical property, Ion beam mixing, SiC/Maxthal coating

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1. 目的

Modification of optical properties of sapphire and diamond by implanting Mg and proton (H+) elements respectively and subsequent heat treatment aimed to apply for the coloration when used as gemstones and for the optoelectronic applications as thin films.

Ion beam mixing[1-4] of a thin SiC film/Maxthal film deposited onto Hastelloy X was conducted to enhance the adhesion, aiming at enhancing the corrosion resistance of this materials in sulfuric acid and SO_2/SO_3 vapor environment at the temperature range of 600℃ -950℃ for the nuclear hydrogen production [5].

2. 方法

100 keV Mg^+ ions from 400keV ion accelerator were implanted into colorless sapphires with a dose of about 1×10^{17} ions/cm^2 and 2MeV H^+ ions using 3MV Tandem accelerator were implanted into diamonds with a dose of about $5x10^{16}$ ions /cm^2. Post-irradiation annealing at 600℃- 1000℃ were conducted in air for sapphire and in vacuum for diamond atmosphere for 2-24 hours. First-principles density-functional theory (DFT)[6] calculations were done to predict the band gap variation of the Mg sapphire.

Hastelloy X sheets with dimension 20x20x0.5 mm were polished by diamond paste upto 1 micron on both sides using the standardized metallographic technique. And then, the sputter cleaning of the coupons was performed for 10 minutes with N ion energy of ~10 keV. After completing the evaporative deposition of Maxthal and SiC films, the coupons were ion-beam-mixed at Takasaki with N+ energy 200 keV. In this work we have coated three coupons (20x20x0.5 mm) of Hastelloy X by Maxthal 211 by e-beam evaporation under high vacuum conditions. Detailed descriptions on the specimens are shown in Table 1. All the samples after the necessary processing were cut into suitable dimensions for X-TEM analyses. For the cross-sectional analyses, the field emission transmission electron microscope (model FB-2100F) manufactured by JEOL Ltd was used. For X-TEM analyses, the specimens were prepared by a focused ion (Ga+) beam.

３．研究成果

Fig. 1 is a photo of green colored diamonds produced by 2MeV proton (H^+ ion) implantation with a dose of $5.5x10^{16}$ ions/cm^2. The original colors of the diamond before the irradiation were brown and light brown and these colors change into dark green [Fig. 1(a)] and green [Fig. 1(a)]. The difference is not so vivid visually but recognizable only when exposed to a bright light source. The 2 MeV proton irradiated diamond turned to near-red color by subsequent annealing at 600℃ in vacuum for 2 hours (Fig. 2). So, the difference caused by original diamond color becomes clear. On the other hand, the dose effect on the color density was not so distinctive above $5X10^{16}$/cm^2. Further decrease in the proton dose may be required for the color density reduction of the green diamond.

Mg ions implantation with a dose of $1x10^{17}$ions/cm^2 turned the colorless sapphire into brown [Fig. 3 (b)]. The brown color disappears and turned to original white color after the annealing at 900℃ for 4 hours[Fig. 3 (c)].

Fig.4 shows the calculated results of density of states (DOS) [6] of a white sapphire (a) and Mg doped sapphire (b). This calculation implies that optical property of sapphire is varied depending on the dopant species.

Fig. 5 shows the X-TEM of Maxthal and SiC coated and ion-beam-mixed Hastelloy X specimens with the film thicknesses around 2000 Å each. It is found that the processing resulted in the smooth morphology at the interface. The cross section energy dispersive spectroscopic analyses revealed the presence and accumulation of nitrogen ions on Maxthal side of the Maxthal / Hastelloy X interface and the Hastelloy X substrate was found with the recoiled Al ion implants in the area adjacent to the Maxthal film. The high resolution point EDS analyses exhibits the concentration N in Maxthal side is about 10 atomic % and Al in Hastelloy X side about 0.35 atomic %.

In Fig. 6, we see X-TEM image of the Maxthal filme/Hastelloy X coupon with the film thicknesses around 3000 Å. It is found that interface of as-coated Hastelloy X substrate is rough and undulating in comparison to that observed in the IBM sample. Maxthal film was found with varying amounts of oxygen present through its thickness. Quantitatively more oxygen was found close to the interface of Hastelloy X and Maxthal than the quantity of oxygen found in the surface of the film.

In case of coupons that were coated with 1000Å Maxthal and 2000Å SiC films, the ion (N+) beam mixing at 200 keV did not show very different behavior than that observed where both films were 2000 Å each. EDS and X-ray mapping analyses at the coupon's cross-section also revealed the Al recoil implantation into substrate regime near the boundary. Oxygen in varying amounts was found through thickness in Maxthal and SiC films.

4．結論・考察

In our previous study, we obtained the reddish color diamond as the result of proton (H^+ ion) irradiation and subsequent annealing at 600℃ in vacuum for 2 hours. We thought that the dark green color of proton irradiated diamond resulted from the too large dose of proton and the reduced dose will result in the lighter green color. We have found the color density is not so much different in this dose range as observed visually. However, the original color affects the density of the green color. When a certain impurity atoms are included in a natural diamond, the diamond is colored, for example, a brown colored diamond is due to N impurity. However, a 2 MeV proton irradiation turned the color into green regardless the original color. It seems the darker green diamond is produced as the more impurity exists in the pristine diamond.

Through the implantation of Mg into colorless sapphire we cam expect an appearance of a new color due to the possible band structure modification. Mg implantation and then subsequent annealing produces brown color, but the brown color recovers to the original colors after the annealing at 900℃ in the air. According to the DOS calculation, Mg doping in sapphire should produce a different color as shown in Fig. 4, however, we find visually no change in the annealed Mg implanted sapphire, implying that a different elemental doping does not always seem to produce different colors. We are trying to understand this result using XPS and XRD. Further study will be reported later.

For the ion beam mixing, overall it may be said that the IBM treatment of SiC overcoat on Maxthal on Hastelloy X can bring about several advantages such as a reduced abruptness of the interface due to their comparable CTEs (that subsequently can leave the coated structures in less residual stresses) and an enhanced adhesion thereby protecting the SiC film's detachment from the substrate at high operating temperatures encountered in S-I cycle. Depending e.g., on the thermodynamic effects, new alloy micro-phases can also result that may be considered important for the good bonding strengths.

In summary, a proton-irradiated diamond showed green color emission and then modified to yellow color upon the post irradiation annealing. Mg ion implantation into blue and colorless sapphires changed the color into brown but the post-implantation annealing return the color to the original ones. The cross section energy dispersive spectroscopic analyses of N ion implanted SiC(2000Å)/Maxthal(2000Å)/Hastelloy X substrate specimen revealed the presence and accumulation of nitrogen ions in Maxthal side and of Al atoms recoil-implanted from Maxthal film in Hastelloy X side, implying that the ion beam mixing occurred. In case of coupons that were coated with 1000A Maxthal and 2000A SiC films, the ion (N+) beam mixing at 200 keV did not show very different behavior than that observed where both films were 2000A each.

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(a) (b)

Fig. 1 Photos of green colored diamonds produced by 2 MeV proton implantation with a dose of 5.5×10^{16} ions/cm^2: (a) Originally brown color changes to dark green. (b) White brown diamond turned into green color of lower density.

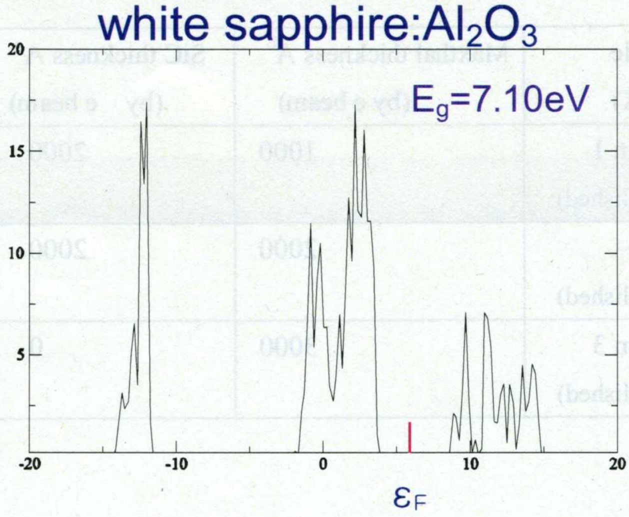
(a) (b)

Fig. 2 Photos of reddish diamonds produced by proton irradiation and subsequent annealing at 600℃ in vacuum for 2 hours: (a) dark green changes to strong reddish color. (b) white brown diamond shows brighter and rather brownish color.

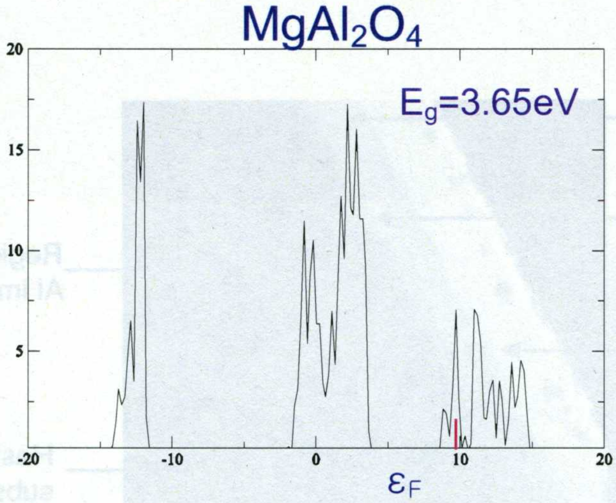
(a) (b) (c)

Fig. 3. Mg ion implantation on a colorless sapphire: (a) the prepared sapphire is colorless and transparent. (b) 100 keV Mg ions are implanted onto the colorless sapphire with a dose of 1.0×10^{17} and turn the sapphire brown. (c) the brown color disappear after the annealing at 900℃.

2007B−C15



(a)



(b)

Fig. 4. Calculated results of density of states (DOS): (a) white sapphire and (b) Mg doped sapphire doped sapphire. A large underestimation (~20%) of the band gap compared to the experimental value is the well-known shortcoming of the LDA. This calculation implies that optical property of sapphire is varied as a function of the dopant.

2007B−C15

Table 1: Processes and materials used for coating formation and ion mixing

Sample (Hastelloy X)	Maxthal thickness A° (by e beam)	SiC thickness A° (by e beam)	Ion beam mix IBM
Coupon 1 (diamond polished)	1000	2000	N+ 200 keV
Coupon 2 (diamond polished)	2000	2000	N+ 200 keV
Coupon 3 (diamond polished)	3000	0	Not done

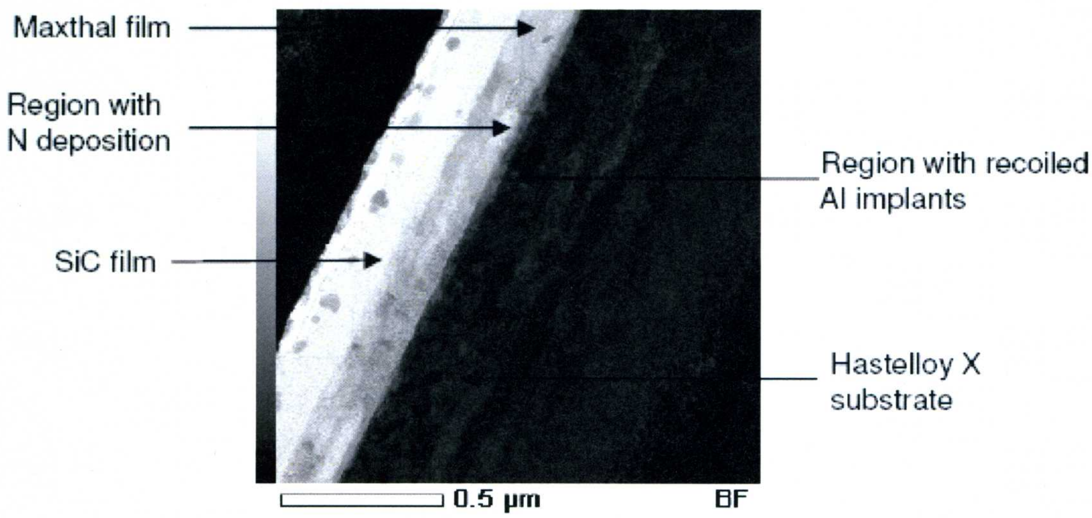


Fig. 5. XTEM image of Maxthal and SiC coated and ion beam mixed Hastelloy X coupons with the film thicknesses 2000 A each. HR EDS revealed the concemtration of N is about 10 at% and that of N is about 0.35 at%.

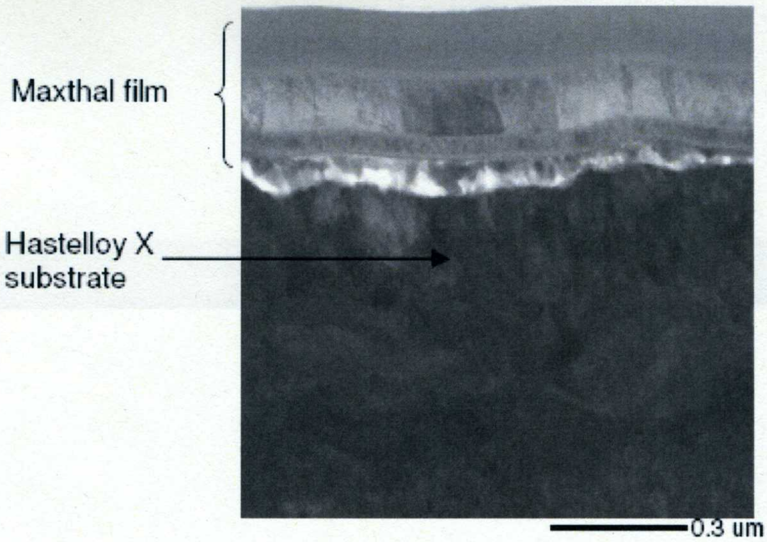


Fig. 6. X-TEM image of Maxthal coated Hastelloy X coupons with the film thicknesses ~3000 A.