

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

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Proton-irradiated diamond showed green color emission and then modified to yellow color after the post irradiation annealing. A blue color emission by Co ion implantation into white sapphire was quite reproducible after a post implantation annealing and the optical density increases as a function of the ion dose. SiC film deposited onto Hastelloy X with an ion beam mixing was sustainable up to 1000°C in air, in which we found an interfacial reaction to form Ni-Si compounds which may act as a functionally graded layer.

キーワード: Proton irradiation, Ion implantation, Optical property, Ion beam mixing  
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## 1. 目的

Modification of optical properties of sapphire and diamond was studied by implanting Co and proton (H+) elements respectively and subsequent heat treatment. The application areas of this research include the coloration when used as gemstones and optoelectronic applications as thin films. To understand the change in optical properties, calculations of the band structure using first principle density functional theory (DFT) were preceded. And, characterizations of surface chemical properties before and after the ion implantation and subsequent annealing were conducted.

Ion beam mixing<sup>1-3)</sup> of thin ceramic films deposited onto Ni-based alloys such as Hastelloy X is conducted to enhance the adhesion, aiming at increasing the corrosion resistance of this materials in sulfuric acid and SO<sub>2</sub>/SO<sub>3</sub> vapor environment at the temperature range of 600°C-950°C for the nuclear hydrogen production<sup>4)</sup>.

## 2. 方法

100 keV Co+ ions from 400keV ion accelerator were implanted into the sapphire (Co+) with a dose of about  $1 \times 10^{17}$  ions /cm<sup>2</sup> and 1-2MeV H+ ions using 3MV Tandem accelerator were implanted into diamond (H+) and ruby (H+) samples with a dose of about  $5 \times 10^{16} - 1 \times 10^{17}$  ions /cm<sup>2</sup>. Post-irradiation annealing at 600°C- 1000°C were conducted both in air and in vacuum atmosphere for 2-24 hours. Visually observed changes in the optical properties of the treated diamond, ruby and sapphire specimens have been and are being analyzed with XPS, Raman and FTIR spectroscopies to understand the mechanisms of the changes. First-principles density-functional theory (DFT)<sup>5)</sup> calculations were done to predict the band gap variation of the doped diamond and sapphire and then to choose the ion specie.

About 50, 100, and 150 nm thick SiC coating layers on Hastelloy X (Ni49-Cr22-Fe16) were conducted, and then

150 keV N ions were implanted in order to obtain the best suitable initial-coating layer thickness on the substrates. After heating at 900 °C, the interfacial reactions were analyzed with cross-sectional SEM observation with EDS and AES line-scan techniques across the interface.

### 3. 研究成果

Fig. 1 is a photo of green colored diamond produced by 2MeV proton ( $H^+$  ion) implantation. We find there is no appreciable difference between 1 MeV and 2 MeV. Only the proton dose can affect the optical density. The 2MeV proton irradiated diamond turned to near-red color by subsequent annealing at 600°C in vacuum for 2 hours (Fig. 2). We found a reduction in the optical density of ruby by proton irradiation followed by annealing. The characterization of the proton irradiated ruby has not been finished. Fig. 3 shows a sky-blue color emission of a Co implanted originally transparent sapphire after post-implantation annealing at 1000°C in air for 6 hours.

In the previous experiment, we also obtained a blue sapphire by 100 keV Co ion implantation with a dose of  $1 \times 10^{17}/\text{cm}^2$  and subsequent annealing at 900°C. In this experiment, the other(non-irradiated) side of the Co implanted blue sapphire was implanted with Co ions with a dose of  $1 \times 10^{17}/\text{cm}^2$ . This sample shows more sky-blue color emission after post-implantation annealing at 1000°C.

Fig.4 shows the calculated results of density of states (DOS)<sup>5)</sup>: (a) white sapphire, (b) Co doped sapphire, (c) Mg doped sapphire, and (d) Cu 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 depending on the dopant species. The doping effects can be qualitatively evaluated by an optical observation.

The SiC film deposited on Hastelloy X substrate is not detached from the substrate even at the elevated temperature above 900 °C (Fig.5-a and -b) when the ion beam mixing is applied at the early stage of the deposition. The SiC film deposited on Hastelloy X substrate is easily peeled off without the ion beam mixing (Fig 5c). Depending on the film thickness, the colors of the SiC film appear differently (Fig 5a and - b). In this work, 150 keV N ions were irradiated onto the 50nm, 100nm, and 150nm thick SiC film. All three samples showed no detachment of SiC film after depositing about 1 μm thick SiC film additionally and then heating to 900°C. However, the most appropriate film thickness of SiC for IBM at 150 keV is still under investigation. For this study, we compare the SRIM calculation with Auger elemental mappings at the interface.

IBM SiC/Hastelloy-X was thermo-cycled at 400-900°C in air. Theoretically, the film should be peeled-off due to a huge difference of CTE (more than 3 times at 900°C), however, the IBM film remains unpeeled (Fig. 6). The IBM SiC film sustains even at 1000°C and shows no corrosion in  $H_2SO_4$  at 300°C for 2h. Cross-sectional back scattered electron(BSE) images of IBM SiC/Hastelloy-X without heating and with heating at 900°C in air are shown in Fig 7. The interface between SiC film and Hastelloy X of non-IBM sample is clearly seen in Fig. 7a while the interface of IBM and heat-treated sample is not clear (Fig. 7b). These observations suggest us a possibility of the interfacial reaction between SiC film and Hastelloy X substrate. To investigate the interfacial reaction products X-ray diffraction was employed. Fig. 8 shows various XRD peaks within the diffraction volume: Firstly, XRD peaks relating to Hastelloy X and SiC can be

identified as shown in Fig. 8. Except for these peaks, we see the many unidentified peaks. Some of the unknown peaks should be associated with  $\text{SiO}_2$  coexisting with SiC in the film and the other unknown peaks seem to be associated with interfacial reaction products such as Ni-Si compounds<sup>6)</sup>. The identification is still progressing.

#### 4. 結論・考察

In our previous study, the purple-red color diamond was obtained as a result of a proton ( $\text{H}^+$  ion) irradiation and a subsequent annealing at  $600^\circ\text{C}$  in vacuum for 2 hours (Fig. 1). Previously, the as-irradiated diamonds looked almost black. We think the previous irradiation dose of proton is too much to see the green color emission of diamond. In this work, the irradiation dose was not so uniform in the irradiation area (1.2cm x 1.2cm). The diamond located closer to the edge of the irradiated area looks less irradiated because the green color was emitted after an irradiation. After annealing the green diamond at  $600^\circ\text{C}$  for 2hrs in vacuum, the color changed from green to yellow-red. It is found that a darker green diamond turned to a more red color emission, while a lighter green diamond may be changed to a lighter yellow diamond.

In Fig. 3, very dense blue color of sapphire is shown. For this, the other (non-irradiated) side of the Co implanted blue sapphire was implanted with the same condition. We performed the heat treatment at  $900^\circ\text{C}$  for 6 hrs as done before, however, the color was not completely changed to blue and the dark area due to ion irradiation was still remained. Subsequent  $1000^\circ\text{C}$  annealing turned an incomplete sapphire to a complete sky-blue color, implying that the color change is controlled by a diffusion process.

Fig.4 shows the calculated results of DOS of white sapphire, Co doped sapphire, Mg doped sapphire, and Cu doped sapphire. This calculation is based on the previously studied X-ray photo-electron spectroscopy (XPS) analysis of the Co implanted sapphire, in which Co2p XPS peaks obtained from as-implanted and post-implantation annealed sapphire samples showed clearly that the metallic Co disappeared in the post-implantation annealed sample. The XPS peak suggested us that Co forms  $\text{CoAl}_2\text{O}_4$  in sapphire. Therefore, we assumed a chemical binding state of metallic elements in the sapphire ( $\text{Al}_2\text{O}_3$ ) as shown in Fig 4 and then calculations were conducted. The calculated results suggest us that the different elemental doping plays a major role in the optical property change. However, a different elemental doping not always seems to produce different colors. More studies are needed in this area.

The reason why the SiC film deposited on Hastelloy X substrate is not detached from the substrate even at the elevated temperature above  $900^\circ\text{C}$  (Fig. 5-a and -b) when the ion beam mixing is applied at the early stage of the deposition is due to the interfacial reaction to form Nickel silicides at the interface, because the substrate consists of mainly 49%Ni, 22%Cr and 16%Fe. The formation of  $\text{Ni}_2\text{Si}$  at the interface of Ni film/SiC substrate was previously studied.<sup>5</sup> The fact that SiC film deposited on Hastelloy X substrate is easily peeled off without the ion beam mixing (Fig 5c) suggests us that IBM plays a role of keeping the SiC film and Hastelloy X substrate in touch during heating until the interfacial reaction occurs. 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. The ion stopping range will be within the film when the film is too thick whereas the peak ion stopping range will be in the substrate when the film is too thin,

resulting in less mixing at the interface in both cases. Therefore, an effort should be paid to find a suitable film thickness so that the maximum intermixing effects could be obtained. In this work, 150 keV N ions were irradiated onto the 50nm, 100nm, and 150nm thick SiC film. We expect that studies on a comparison between the SRIM calculation with Auger elemental mappings at the interface will provide us with a proper condition. The result of this study will be reported later on.

It is manifest that an occurrence of the interfacial reaction generates a new phase at the interface as can be seen in Fig. 8. From the XRD peaks, we can identify Hastelloy X and SiC peaks easily. However, we see the many unidentified peaks. Some of the unknown peaks should be associated with SiO<sub>2</sub> coexisting with SiC in the film and the other unknown peaks seem to be associated with interfacial reaction products. A possible interfacial reaction product can be Ni<sub>2</sub>Si<sup>6)</sup>. A detailed study will be reported later on.

In summary, a proton-irradiated diamond showed green color emission and then modified to yellow color upon the post irradiation annealing. A blue color emission by Co ion implantation into white sapphire was quite reproducible and it is found that the optical density increases as a function of the ion dose. Ion beam mixing is working well for the adhesion enhancement of SiC film deposited onto the Ni-based alloys. SiC film deposited onto Hastelloy X with an ion beam mixing was sustainable up to 1000°C in air, in which we found an interfacial reaction to form Ni-Si compounds which may act as a functionally graded layer.

## 5. 引用(参照)文献等

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Fig. 1 Photo of a green colored diamond produced by 2 MeV proton ( $H^+$  ion) implantation.



Fig. 2 Photo of a yellow-red diamond produced by proton ( $H^+$  ion) irradiation and subsequent annealing at  $600^{\circ}C$  in vacuum for 2 hours.

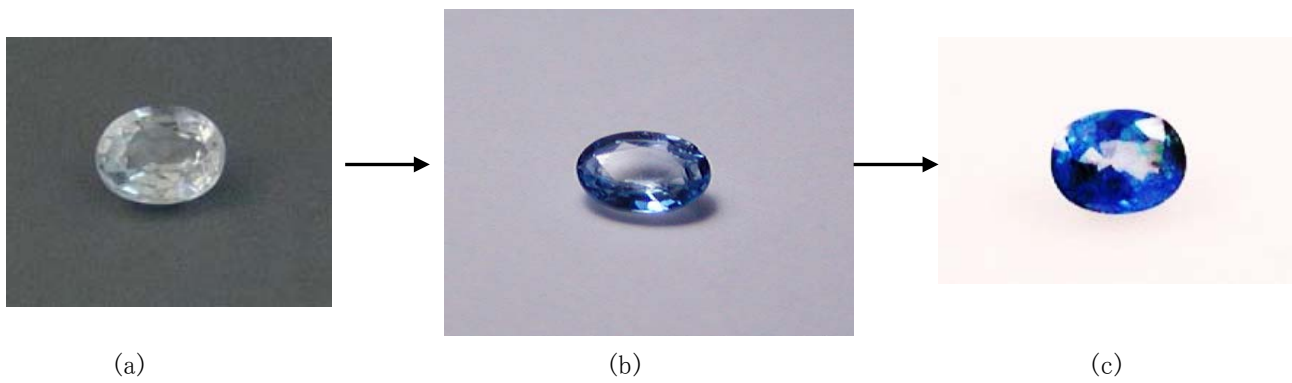


Fig. 3. A blue sapphire by 100 keV Co ion implantation on the other (non-irradiated) side of the Co implanted blue sapphire: This sample shows more sky-blue color emission after post-implantation annealing at 1000°C (c).

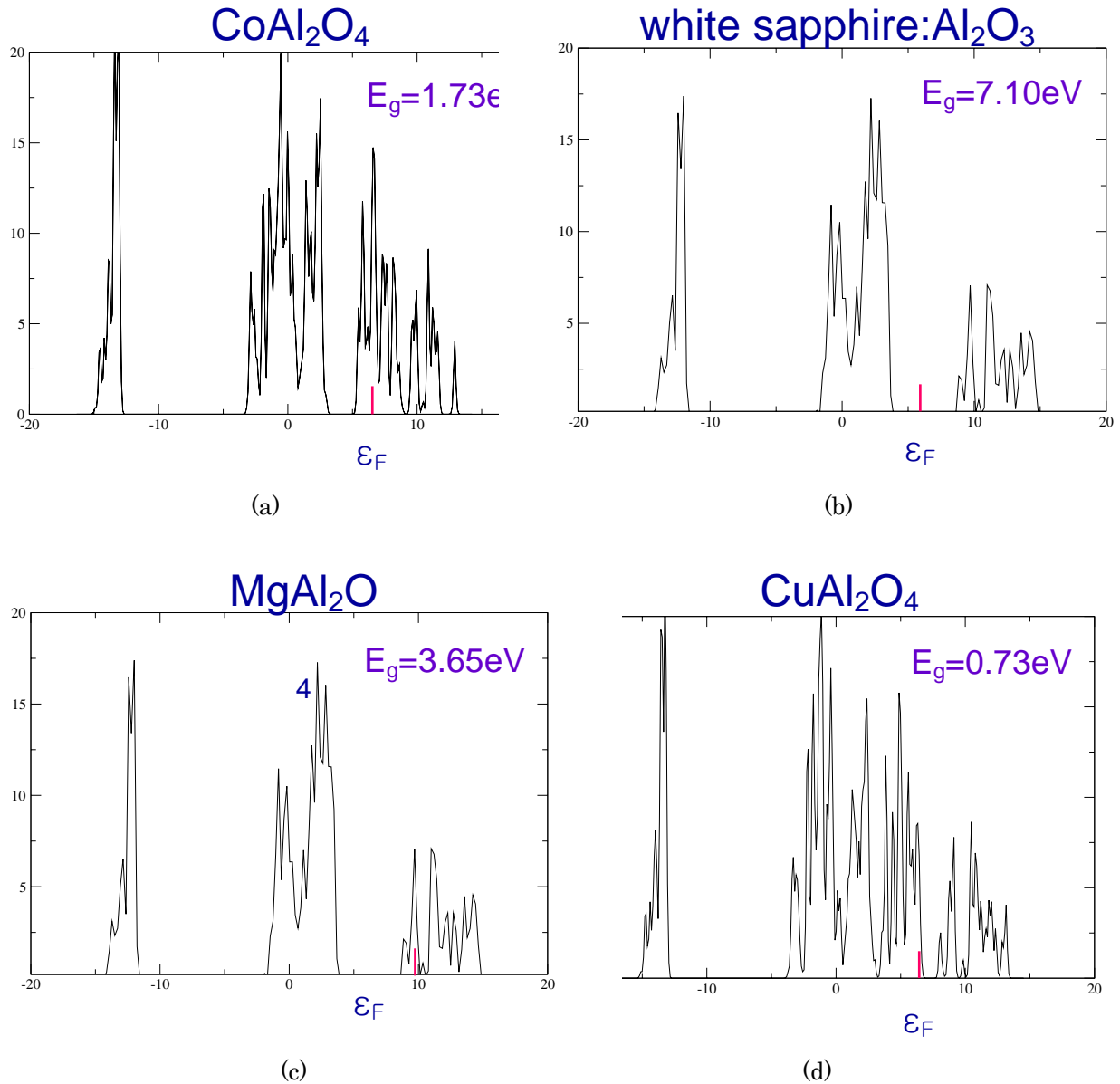


Fig. 4. Calculated results of density of states (DOS): (a) white sapphire, (b)Co doped sapphire, (c) Mg doped sapphire, and (d) Cu doped sapphire. A large underestimation ( $\sim 20\%$ ) of the band gap compared to the experimental value is the well-known shortcoming of the LDA. This calculation implies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

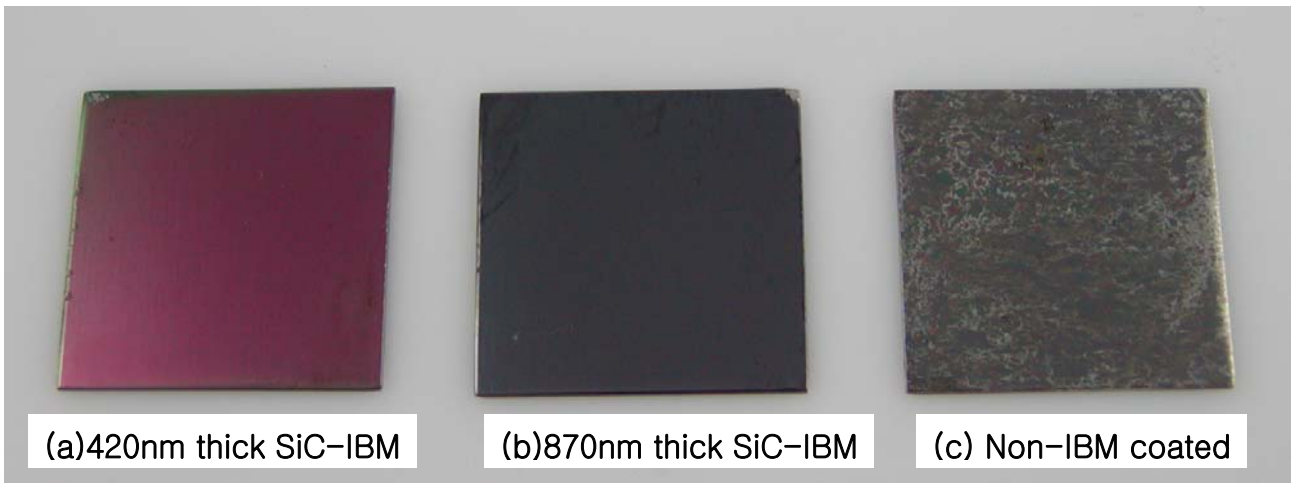


Fig. 5. The SiC film deposited on Hastelloy X substrate is not detached from the substrate even at the elevated temperature of above 900°C (a, b) if the ion beam mixing is applied at the early stage of the deposition coated layer. The SiC film deposited on Hastelloy X substrate is easily peeled off without the ion beam mixing (c). Depending on the film thickness, the colors of the SiC film appear differently (a, b).

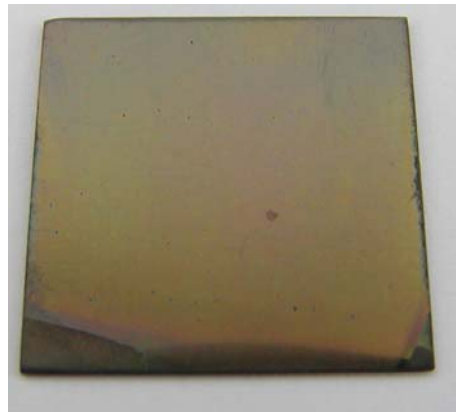


Fig 6. IBM SiC/HA-X thermo-cycled at 400–900°C in air: The film should be peeled-off due to a huge difference of CTE at 900°C, however, the IBM film remains unpeeled.



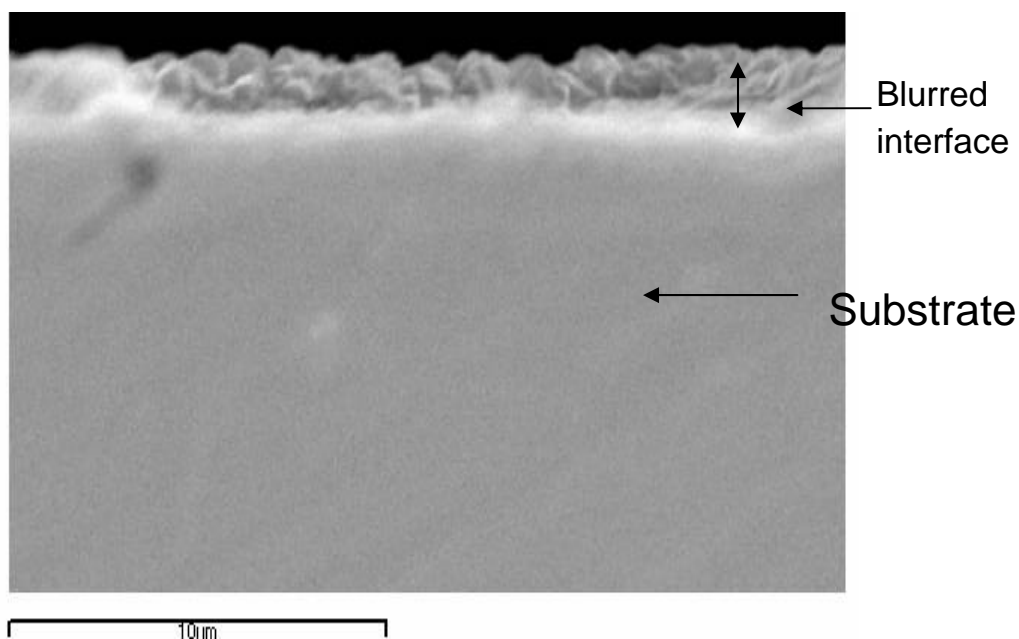
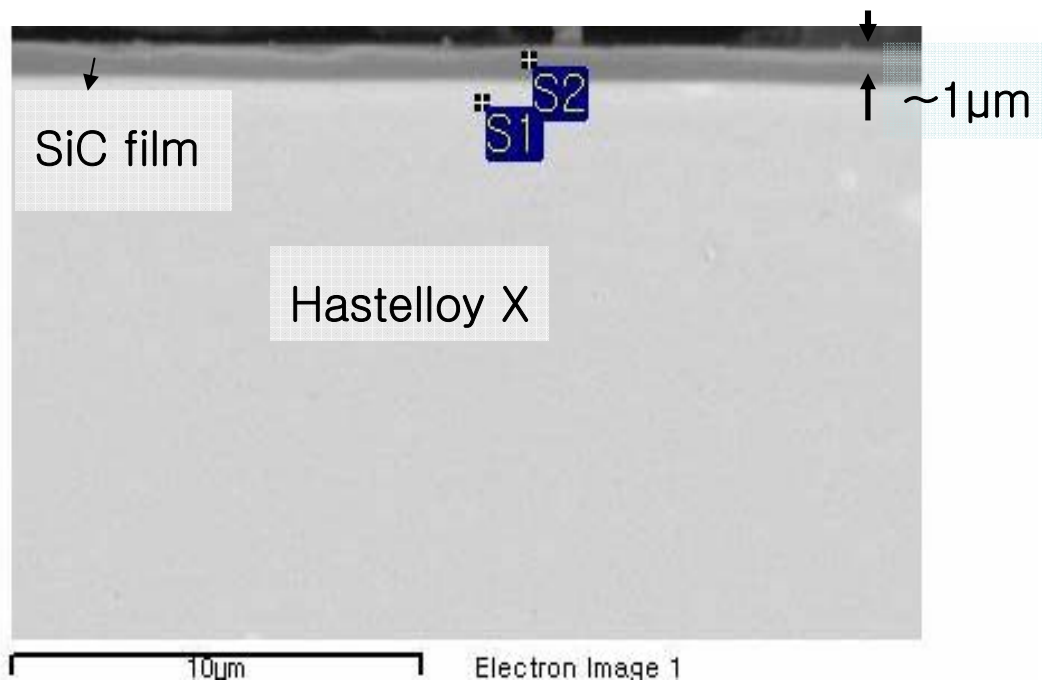


Fig. 7. Cross-section BSE Image of IBM HX/SiC without heating and with heating at 900°C in air.

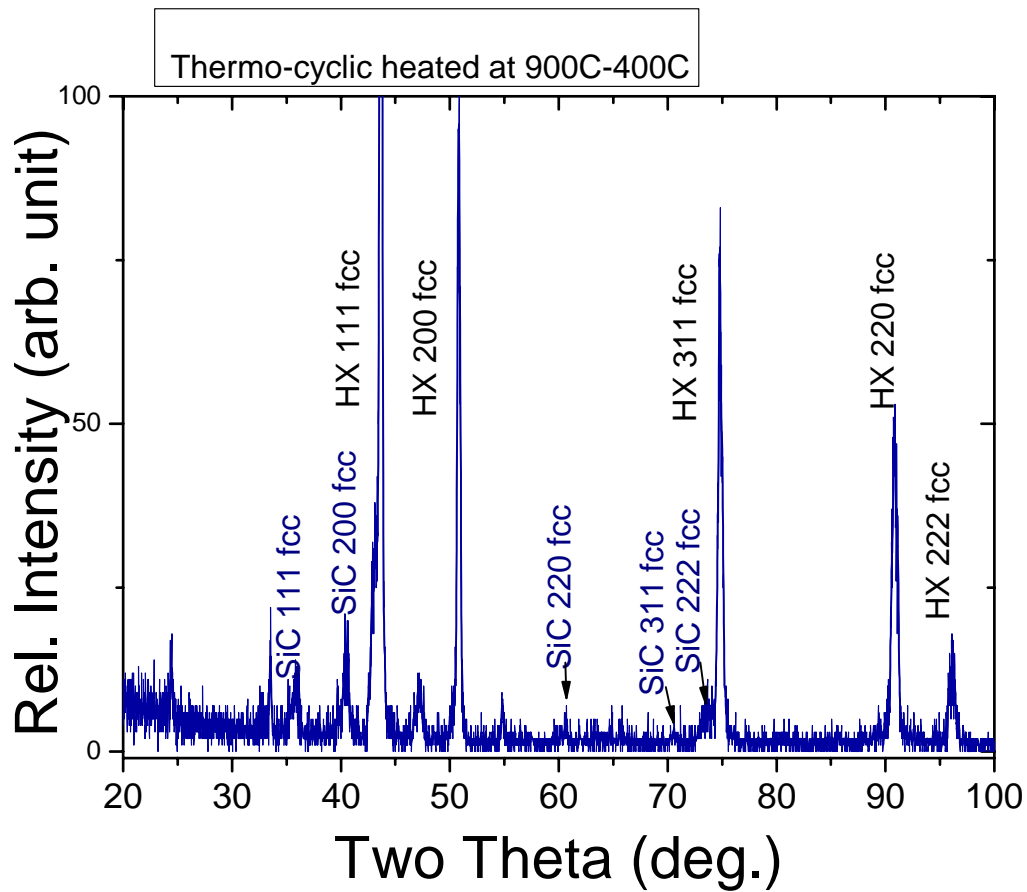


Fig. 8. XRD of the thermo-cyclic heated SiC/Hastelloy X suggests many unknown peaks except for peaks corresponding to Hastelloy X and SiC. Some of the unknown peaks should be associated with SiO<sub>2</sub> coexisting with SiC in the film and the other unknown peaks seem to be associated with interfacial reaction products such as Ni-Si compounds.