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Low Energy Indium or Gallium Ion Implantations to SiO_2 Thin Films for Development of Novel Catalysts[*]

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In an earlier paper [S. Yoshimura *et al.*, Appl. Surf. Sci. **257**, 192 (2010)], it has been demonstrated that indium (In) implanted silicon dioxide (SiO_2) thin films catalyze a reaction of benzhydrol with acetylacetone. In this study, it is found that the threshold In ion incident energy for manifestation of the catalytic effect exists between 400 and 470 eV. Furthermore, a technique to implant gallium (Ga) to SiO_2 films has been developed with highly controlled doses and injection energies for the formation of thin films that promote Ga catalysts. The efficiency of catalytic reactions by Ga implanted SiO_2 thin films is yet to be improved. Unlike In implanted SiO_2, the reason why no significant reaction was observed in the case of Ga implanted SiO_2 films examined in this study seems that the Ga ion energy was so low that deposited surface Ga atoms should lack interactions with Si atoms for the manifestation of catalytic reaction. [DOI: 10.1380/ejssnt.2014.197]

Keywords: Ion implantation; Indium; Gallium; Catalysis

I. INTRODUCTION

Recently indium (In) included materials have been reported to function as chemical catalysts [1–3]. Especially, catalytic effects induced by interactions between In and silicon (Si) have attracted much attention [1, 2]. In earlier papers [4–7], we have proposed an experimental method in which implantations of metal ions such as In into Si containing materials by ion beam injection is useful for preparing such catalytic materials.

In Ref. [4], we reported that In implantation into silicon dioxide (SiO_2) thin films catalyzed a reaction of benzhydrol with acetylacetone. Surface analyses of In implanted SiO_2 films show the presence of a +3 valence In [In(III)] compound formed on the surfaces [6]. Our subsequent study [6] also examined whether the catalytic properties depended on the injection energy: In ions were injected into SiO_2 films at different kinetic energies of 50, 100, 200, and 470 eV. It was then found that the catalytic effect was evident only when the ion energy was 470 eV and the ion dose was 1×10^{17} ions/cm^2. However, the threshold energy of catalytic effect manifestation was not identified yet. In this paper, we firstly examine the catalytic effect of a 400 eV In injected SiO_2 film in order to investigate the threshold energy.

Secondly, we attempt to develop new catalysts by implanting gallium (Ga) ions into SiO_2 thin films. In this study, Ga ions are injected into SiO_2 films in the energy range of 100-470 eV and the ion dose range of 10^{16}-10^{18} ions/cm^2. A novel type of Ga catalysts is highly desirable because they accelerate many organic chemical reactions. In various chemical reaction systems [8–16], Ga is known to have better catalytic effects than In and therefore we expect that Ga implantation into SiO_2 thin films may also exhibit better catalytic effects than In implanted SiO_2 films. Generally, the properties of Ga(III) are similar to those of In(III) because both belong to group 13 metals. However, unlike In, enhancements of catalytic ability by the interaction between Ga and Si have not been reported yet. Therefore, as a starting point, we examine whether Ga implanted SiO_2 thin films would catalyze the reaction of benzhydrol with acetylacetone in this study.

II. EXPERIMENTAL SETUP

The ion beam production experiment was carried out using a low-energy mass-selected ion beam system [17]. The system consists of an ion source, an extractor electrode, a mass selector, a decelerator, and a process chamber (Fig. 2 of Ref. [17]). The configuration of the modified Freeman-type ion source was shown in Figs. 1 and 2

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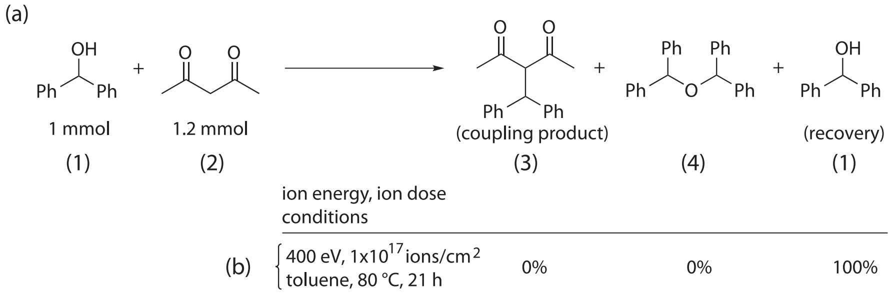

FIG. 1: (a) The reaction of (1) benzhydrol and (2) acetylacetone produces (3) the coupling product and (4) bis(diphenylmethyl) ether. (b) Yield of reactions in the presence of In implanted SiO_2/Si substrate. The incident In ion energy was around 400 eV. The In ion dose was 1×10^{17} ions/cm^2.

of Ref. [18]. In the In or Ga ion beam experiments, we used In_2O_3 or Ga_2O_3 as sputtering targets. In the arc chamber (25.4 mm in diameter, 50.8 mm in length) of the ion source, an Ar plasma was generated by a hot tungsten wire and In or Ga atoms were sputtered from In_2O_3 or Ga_2O_3 targets by the plasma. The targets were typically biased at −500 V for efficient formation of In or Ga ions. In the arc chamber, we had Ar ions, sputtered In or Ga ions, and impurity ions. Among various ions extracted from the ion source by a high voltage of −15 kV applied to the extractor electrode, In or Ga ions were selected by the magnetic-field-based mass selector. In or Ga ions were then directed to the process chamber and decelerated by the decelerator. The kinetic energy of incident ion was in the range of 50 to 500 eV in the present experiments.

In the process chamber, a substrate holder and a mass-energy analyzer (BALZERS, model: PPM-421) were installed and either of them was set on the direct path of the ion beam. The mass-energy analyzer PPM-421 was placed behind the manipulator on which the substrate holder was mounted. The substrate holder was connected with an ammeter (KEITHLEY, model: 485) for the ion beam current measurement. The temperature of substrate was initially set at room temperature but not actively controlled during the ion beam injection experiments. The degree of vacuum in the process chamber was 5×10^{-7} Pa.

In the In or Ga ion beam experiments, the experimental procedure was as follows. Firstly, we measured the mass spectrum of a plasma in the ion source by varying the current to generate the magnetic field of the magnetic-field-based mass selector. Secondly, with an appropriate adjustment of the mass selector, In or Ga ion beams were selected and their mass and energy distributions were measured by PPM-421. For the subsequent experiments, a SiO_2 thin film that had been formed thermally on a Si substrate (SiO_2/Si substrate) was set on the substrate holder. The typical thickness of the SiO_2 layer was 0.1 μm. In or Ga ion beams were injected into the substrates with different energies. The ion dose was evaluated from the ion beam current and the duration of ion injection. Once In or Ga implanted SiO_2/Si substrates were formed in this manner, the sample surfaces were analyzed by X-ray diffraction (XRD) (RIGAKU, model: RINT2200), X-ray photoelectron spectroscopy (XPS) (SHIMADZU, model: ESCA-850), and atomic force microscopy (AFM) (JEOL, model: JSTM-4200D). Finally catalytic abilities of the samples were examined.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Indium ion beam experiment

The mass spectrum of ions extracted from the ion source shows that N^+, O^+, Ar^{2+}, Ar^+, In^+, and W^+ ions were present in the ion source [4]. With an appropriate adjustment of the mass selector, we selected In^+ ions as a beam for ion implantation. The mass spectrum of such an ion beam measured by PPM-421 indicates the appearance of only a single peak at the mass number of 115, i.e., the ion beam consists of pure In with no impurity. The energy spectrum of the In ion beam shows that the peak energy was 404 eV and the full width at half maximum (FWHM) of the peaked profile was 5 eV. These results show that the In ion beam was nearly monochromatic. Then, In ion beams were injected into a SiO_2/Si substrate. The In ion dose was 1×10^{17} ions/cm^2. The size of substrate was 1cm×1cm and the area exposed to the ion beam was a disk with a diameter of 0.8 cm.

Catalytic ability of the In implanted SiO_2 thin film was examined for a reaction of benzhydrol with acetylacetone, which has been found to be promoted by catalytic effects of In and Si interactions [19]. The organic chemical reactions were examined in a 10 mL flame-dried two necked round-bottomed flask equipped with a stop cock, a Teflon-coated magnetic stirring bar, and a reflux condenser fitted with a nitrogen inlet adapter. The In implanted SiO_2/Si substrate was broken into 5-10 small pieces and placed in the flask, together with benzhydrol (1 mmol), acetylacetone (1.2 mmol), and toluene (2 mL). The resulting mixture in the flask was heated at 80°C in an oil bath for reaction periods of 21 h. After the reaction, the mixture was cooled to room temperature and treated with H_2O (10 mL) and diethyl ether (10 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give the crude product. Reaction yields were determined by ^{1}H NMR using the internal standard.

Figure 1 shows the reaction result obtained for the In implanted SiO_2/Si substrates with the ion energy of 400 eV. The percentage shown here is the molar distribution. As denoted in Fig. 1(a), the reaction of (1) benzhy-

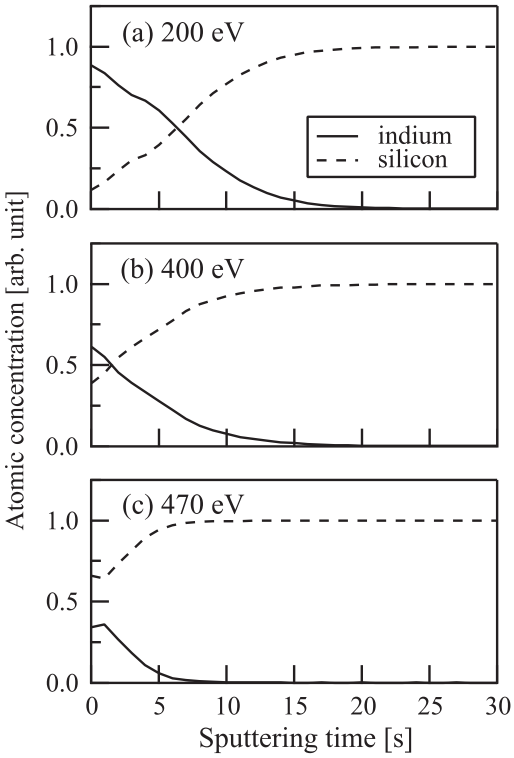

FIG. 2: Depth profile of the atomic concentration of In and Si measured by X-ray photoelectron spectroscopy for In implanted SiO_2/Si substrates. The In ion energies were (a) 200, (b) 400, and (c) 470 eV. The In ion doses were $1{\times}10^{17}$ ions/cm^2 in all cases. An Ar ion beam (600 eV, 50 mA) etching was used to analyze depth profile. When this Ar ion beam was injected to a SiO_2 film, 50.7 nm of SiO_2 was etched in a minutes.

drol and (2) acetylacetone here produces (3) the coupling product and (4) bis(diphenylmethyl) ether. Figure 1(b) shows that in this case no reaction takes place and the original benzhydrol is fully recovered. In an earlier paper [6], we reported the catalytic effect of In implanted SiO_2/Si substrates with the ion energies of 50, 100, 200, and 470 eV. For the substrates created with In ion energies of 50, 100 and 200 eV, no reaction took place and the original benzhydrol was fully recovered [Fig. 4(a)-4(c) in Ref. [6]]. When the In ion energy was 470 eV, the coupling product and bis(diphenylmethyl) ether were obtained in 6% and 38% yields, which clearly showed the catalytic effect [Fig. 4(d) in Ref. [6]]. These results in Ref. [6] and Fig. 1(b) suggest that the threshold ion incident energy for manifestation of the catalytic effect exists between 400 and 470 eV.

XRD results suggest that metallic In surface layers were likely formed in the cases of 50 and 100 eV [Fig. 2(a) and 2(b) of Ref. [6]]. Therefore, it is conceivable that surfaces of the substrates with 50 or 100 eV injections consist of metallic In film and the surface In atoms lack interactions with Si atoms which are necessary for the catalytic effect. Since metallic In alone does not catalyze the organic chemical reaction [4], these substrates do not catalyze the reaction. On the other hand, no clear peak due to In was observed in XRD spectra in the cases of 200, 400, and 470 eV. Sticking probability measurements of In (Fig. 5 of Ref. [6]) show that for the substrates with 200, 400, and 470 eV injections In ions are likely implanted into the subsurface regions of SiO_2 films as the ion energy is high enough that no metallic In deposition takes place.

Three In implanted SiO_2/Si substrates (a)-(c) with (a) 200, (b) 400, and (c) 470 eV ion energies were prepared. The In ion doses of the three substrates were the same ($1{\times}10^{17}$ ions/cm^2). These three substrates (a)-(c) were similar to those used in the catalytic analysis in Fig. 4 of Ref. [6] and Fig. 1. To determine whether no In atoms exist on the surfaces of three substrates (a)-(c), we analyzed these substrates with XPS using MgKα (12 kV, 30 mA). An Ar ion beam (600 eV, 50 mA) etching was used to analyze depth profiles of In in the substrates (a)-(c). Figures 2(a)-2(c) show the evolution of the atomic concentrations of In and Si during the Ar ion beam etching. In the case of the 200 eV substrate (a), the atomic concentration of In is much larger than that of Si at the top surface of substrate (top surface corresponds to sputtering time = 0), as shown in Fig. 2(a). In this case, the substrate surface almost consists of an In film and surface In atoms seem to lack interactions with Si atoms which are necessary for the catalytic effect. On the other hand, Fig. 2(b) and 2(c) show that In atoms coexist with Si atoms on the top surfaces of substrates. In the case of the 400 eV substrate (b), the atomic concentration of In is reduced compared to the substrate (a), however, the atomic concentration of In is still larger than that of Si at the substrate surface, as shown in Fig. 2(b). In the case of 470 eV substrate (c), the atomic concentration of In is smaller than that of Si, as shown in Fig. 2(c). Although the reason why the substrates with 200 and 400 eV injections do not catalyze the reaction has not been clear yet, the experimental observations suggest that appropriate dispersion of In atoms on the top surface of SiO_2 layer is necessary for the manifestation of catalytic effects.

B. Gallium ion beam experiment

Firstly, we measured the mass spectrum of a plasma in the ion source for Ga ion beams. By changing the electric current of the mass selector, the ion current extracted from the ion source was measured by a Faraday cup installed just after the mass selector. Figure 3(a) shows the dependence of ion beam intensity on the mass selector current. In Fig. 3(a), several ion peaks are seen, which are identified by PPM-421 as O^+, Ar^{2+}, N_2^+, O_2^+, Ar^+, and Ga^+ ions. Identification of other peaks was difficult because the ion currents for these peaks were too low.

With an appropriate adjustment of the current in the magnetic-field-based mass selector, we selected a specific ion beam. The mass spectrum of a mass-selected ion beam was measured by PPM-421, which is shown in Fig. 3(b). Figure 3(b) indicates that only a single peak appears at the mass number of 69, i.e., Ga^+ ions with no impurity. An example of the energy spectrum measured by PPM-421 is given in Fig. 4, which shows that, in this specific case, the peak energy is 472.5 eV and the FWHM of the energy distribution is 2.5 eV. These results show that the mass-selected Ga ion beam used in this study was nearly monochromatic.

Following the experiments discussed above, Ga ion

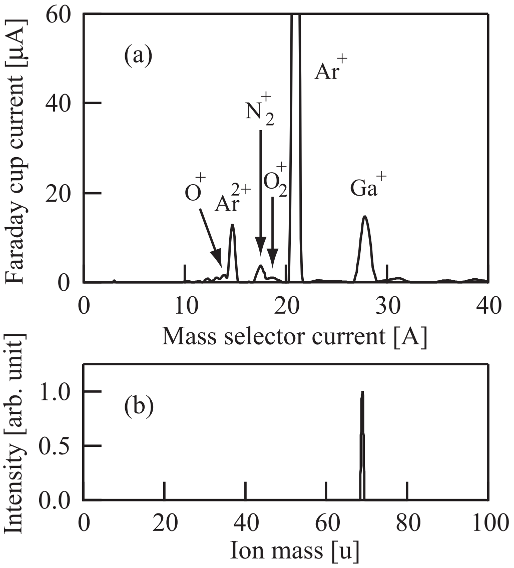

FIG. 3: (a) Ion beam intensities measured by a Faraday cup for each ion species selected by the magnetic mass selector. The horizontal axis represents the current to produce the magnetic field of the mass selector. The figure shows the mass spectrum of ions in the ion source. (b) Mass spectrum of a mass-selected ion beam used in the study. The peak mass number is 69, which corresponds to the mass of Ga.

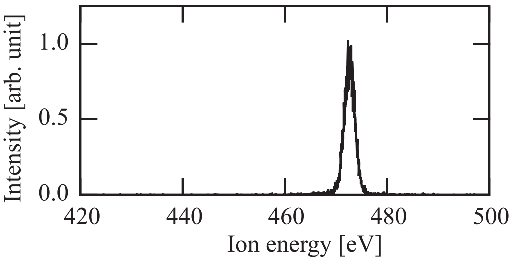

FIG. 4: An example of energy spectrum of Ga ion beam used in this study.

beams were injected into SiO_2/Si substrates. Three Ga injected SiO_2/Si substrates with different ion energies were prepared for surface analyses. The Ga ion beam current used in the experiments was about 1 μA. The ion energies of three substrates (a)-(c) were (a) 100, (b) 200, and (c) 470 eV. The Ga ion doses of all substrates were the same ($1{\times}10^{17}$ ions/cm^2).

Although the surfaces of the Ga implanted SiO_2/Si substrates were analyzed with XRD (θ-2θ method) using Kα_1 of Co ($\lambda = 1.78892$ Å), no clear peak of Ga (e.g., metallic Ga or Ga_2O_3) was observed. To determine whether no Ga atoms exist on the surfaces of substrates (a), (b), and (c), we analyzed the surfaces with XPS. In this study, Ar ion beam etching was used to clean off surface contaminations. The XPS spectra in the Ga $2p$ region for the substrates (a)-(c) are shown in Fig. 5(a)-5(c). In Fig. 5(a) and 5(b), two peaks corresponding to metallic Ga and Ga_2O_3 are observed, indicating that metallic Ga coexisted with Ga_2O_3 on the surface of the substrates (a) and (b). On the other hand, in Fig. 5(c) the only peak corresponding to Ga_2O_3 is seen, suggesting that nearly no metallic Ga remained on the surface of the substrate (c).

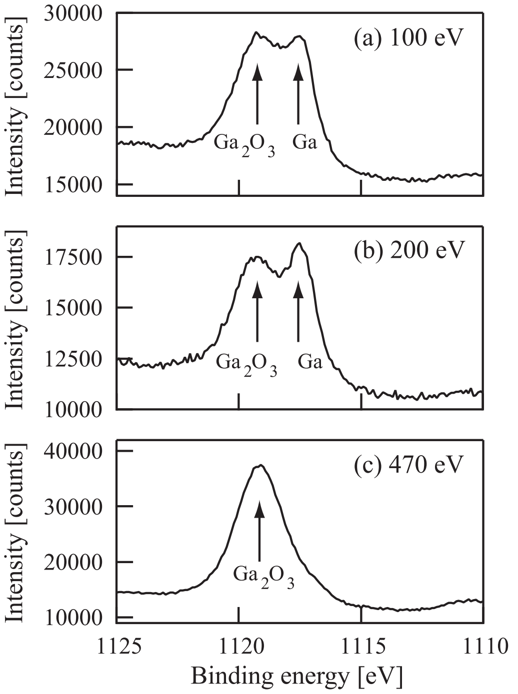

FIG. 5: X-ray photoelectron spectroscopy spectrum in the Ga $2p$ region for Ga implanted SiO_2/Si substrate surfaces. The Ga ion energies were (a) 100, (b) 200, and (c) 470 eV. The ion doses were $1{\times}10^{17}$ ions/cm^2 in all cases.

TABLE I: Yields of the benzhydrol and acetylacetone reactions in the presence of Ga implanted SiO_2/Si substrates formed under different ion beam conditions (a)-(i).

	ion beam condition	coupling product
(a)	100 eV, $1{\times}10^{17}$ ions/cm^2	0%
(b)	200 eV, $1{\times}10^{17}$ ions/cm^2	0%
(c)	470 eV, $1{\times}10^{17}$ ions/cm^2	0%
(d)	100 eV, $1{\times}10^{16}$ ions/cm^2	0%
(e)	200 eV, $1{\times}10^{16}$ ions/cm^2	0%
(f)	470 eV, $1{\times}10^{16}$ ions/cm^2	0%
(g)	100 eV, $6{\times}10^{17}$ ions/cm^2	0%
(h)	200 eV, $6{\times}10^{17}$ ions/cm^2	0%
(i)	470 eV, $9{\times}10^{17}$ ions/cm^2	0%

Atomic-scale morphologies of the surfaces of substrates (a)-(c) were analyzed with AFM, the photographs of which are given in Fig. 6. Figure 6 shows that the substrate surface morphology after Ga ion injection depends on the ion energy. In Fig. 6(a)-6(c), particle-like structures are seen. The size of particle-like structures decreases as the Ga injection energy increases, as shown in Fig. 6(a)-6(c).

Catalytic abilities of the Ga implanted SiO_2 films (a)-(c) were examined for the reaction of benzhydrol with acetylacetone and shown in Table I(a)-I(c). The experimental procedure was described in Sec. IIIA. In contrast to In implanted SiO_2/Si substrates studied earlier, Table I(a)-I(c) show that the yield of the coupling product by the Ga implanted SiO_2 film was null and benzhydrol was fully recovered. In addition, six other Ga implanted

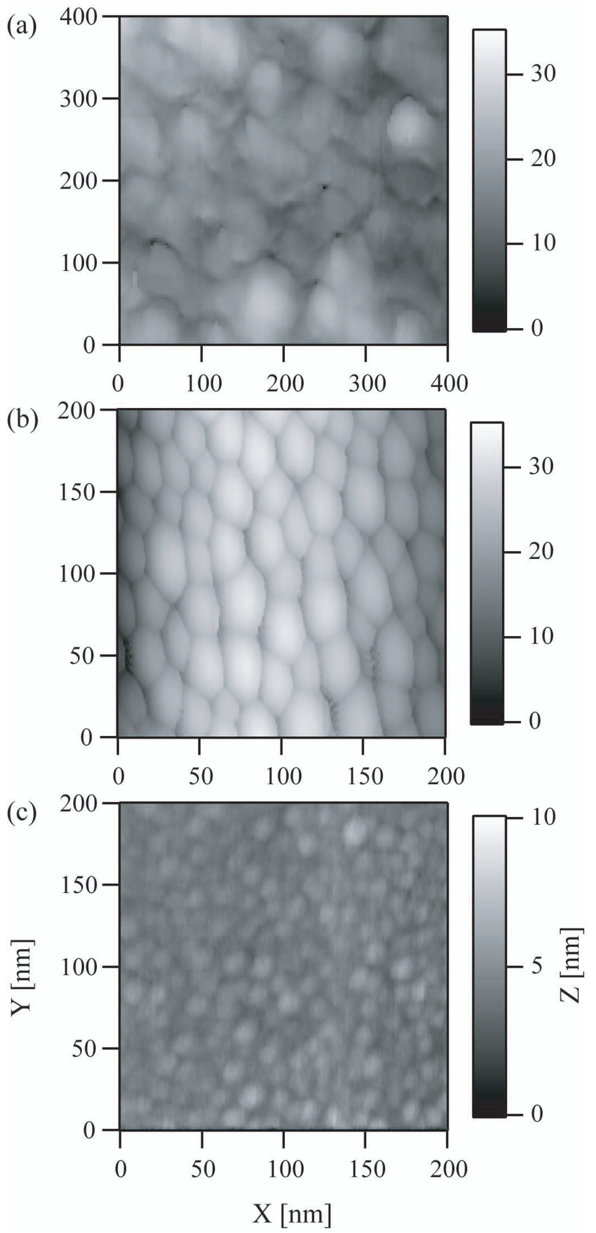

FIG. 6: Atomic force microscopy images of Ga implanted SiO$_2$/Si substrate surfaces. The gray scale on each figure indicates the height in units of nm. The Ga ion energies were (a) 100, (b) 200, and (c) 470 eV. The ion doses were 1×10^{17} ions/cm^2 in all cases.

SiO$_2$/Si substrates with various Ga ion energies and ion doses were also examined, as shown in Table I(d)-I(i). It is found that yields of the coupling products were null in all these cases. Although the ion energies and ion doses of the substrate were similar to those of In implanted substrates in Ref. [6], no significant reaction was observed in the case of Ga implanted SiO$_2$/Si substrates in their energy and dose ranges examined here. These results suggest that, under the current experimental conditions, there is little interaction between Ga and Si that leads to catalytic effects on the reaction examined here.

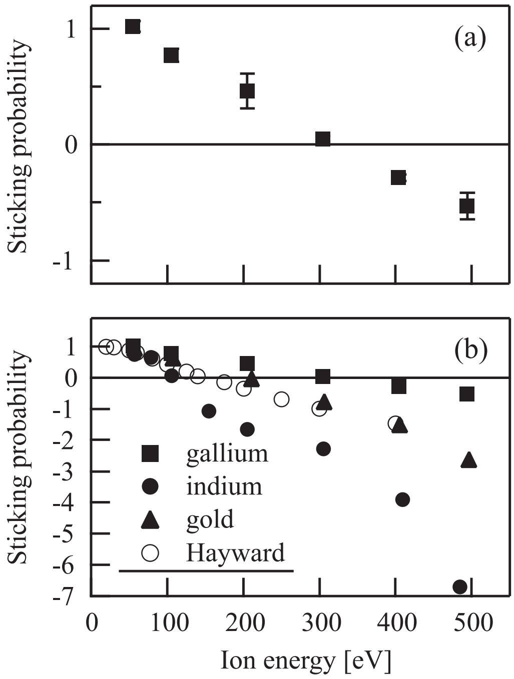

FIG. 7: (a) The measured sticking probabilities of incident Ga ions as a function of the ion injection energy are shown by closed squares. The angle of incidence was normal to the Ga film on the crystal surface. The error bar indicates the standard deviation of the measured data. (b) The measured sticking probabilities of Ga are compared with those of our measured data of In (closed circles) and Au (closed triangles). Sticking probabilities of Au measured by other experimental group (Hayward, et al.) are also shown by open circles.

In order to understand why the catalytic effect of Ga implanted SiO$_2$ thin films was null, we measured sticking probabilities of incident Ga ions on a Ga surface for various ion energies. For the sticking probability measurements, a quartz crystal microbalance (QCM) is mounted in the process chamber. The QCM crystal is a gold-coated AT-cut crystal and has a resonant frequency of 5 MHz. For self-sticking probability measurement, a thin Ga film was formed on a crystal surface by vacuum evaporation before the Ga ion beam injection. The thickness of the Ga film was 2 μm. In the measurement of sticking probabilities, a Ga ion beam with a certain energy was injected into the Ga film formed on a QCM crystal surface. The film mass change on the QCM crystal can be monitored by a QCM controller (ULVAC, model: CRTM-9000). The mass resolution of the QCM system is 2.4×10^{-11} g. For details of the measurement system, the reader is referred to Ref. [20]. With this system, we have measured sputtering yields of MgO [20] and Au [21] by He, Ne, Ar, Kr, and Xe ion beams. The measured sputtering yields of Au and MgO agree well with earlier data obtained by other experimental groups.

The sticking probability is the ratio of the number of deposited atoms to that of incident ions. The number of incident ions can be obtained from the ion beam current measured by the Faraday cup. The number of deposited (or sputtered) atoms can be evaluated from the change in mass of Ga film formed on the crystal surface. As far as we know, sticking probabilities of Ga have not been reported yet. In Fig. 7(a), measured sticking probabilities of Ga are shown as a function of the incident energy by closed squares. In the experiments presented here, the Ga ion incident energy was varied from 50 to 490 eV. The horizontal axis represents the peak energy of ion beam determined by PPM-421. Figure 7(a) shows that the sticking probability decreases monotonically with increasing ion energy and becomes almost zero at the ion energy of about 300 eV. It is also seen that the sticking probability becomes negative in the energy range of 300-500 eV, indicating that Ga substrate is sputtered by the injected Ga ion beam (self-sputtering) in this energy range. In Fig. 7(b), the measured sticking probabilities of Ga are compared with those of In [6] and Au [5] by closed circles and closed triangles, respectively. Figure 7(b) also shows that our measurement of sticking probabilities of Au agrees with those obtained by other experimental group [22]. It is seen that the sticking probabilities of In also monotonically decreases with increasing ion energy. Especially, for ion energy larger than around 100 eV, self-sputtering is shown to take place. Figure 7(b) shows that self-sputtering yields of Ga are much smaller than those of In in the range of 300-500 eV. These results suggest that the reason why no significant reaction was observed in the case of Ga implanted SiO_2/Si substrates in their energy and dose ranges examined here seems to be that the Ga ion energy in this study is so low that the surface Ga atoms lack interactions with Si atoms for the manifestation of catalytic reaction.

IV. CONCLUSIONS

We currently attempt to develop novel catalysts by injecting metal ions into Si containing materials. In this study, ions generated in the ion source were accelerated and then mass selected to produce a pure metal ion beam (in this study, In or Ga ions). The ion beam was then decelerated and injected into the substrate in the energy range of 50-500 eV. The quality of the ion beam was examined by PPM-421. It was confirmed that the ion beam included no impurity ions and the energy distribution was nearly monochromatic. We have used In ion beam injection into SiO_2 thin films to create a material that has both In and Si in close proximity, which exhibits a catalytic effect on an organic chemical reaction [4]. In this study, it is found that the threshold ion incident energy for manifestation of the catalytic effect exists between 400 and 470 eV. The XPS measurements of In implanted SiO_2/Si substrates suggest that appropriate dispersion of In atoms on the top surface of SiO_2 is necessary for the manifestation of catalytic effects. Then, Ga ion beams were injected into SiO_2 thin films, which may become a new type of Ga catalysts in organic chemistry. In contrast to the In implanted SiO_2 thin film, our study on the catalytic abilities of Ga implanted SiO_2 thin films shows that no catalytic effect is observed in their energy and dose ranges examined here. A further study is necessary to determine the experimental conditions for the formation of Ga implanted SiO_2 catalysts. However, we think that the Ga ion beam injection technique developed in this study is useful in developing a catalyst of a thin-film type with highly controlled ion beam dose and injection depths into the substrate.

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