

Dependence of catalytic properties of indium implanted SiO₂ thin films on the film-substrate temperature during indium ion implantation



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ABSTRACT

Chemical substances that contain indium (In) and silicon (Si) in close proximity are known to catalyze certain organic chemical reactions. An earlier paper [Yoshimura, Hine, Kiuchi, Nishimoto, Yasuda, Baba, Hamaguchi, Appl. Surf. Sci. 257 (2010) 192] has demonstrated that In implanted silicon dioxide (SiO₂) films formed at room temperature catalyze a reaction of benzhydrol with acetylacetone. This study, thus, examined effects of substrate temperature during In ion implantation, revealing that, if In ions were implanted into a SiO₂ film at the substrate holder temperature of 200 °C or higher, the film exhibited no catalytic ability. Surface analyses by the X-ray diffraction, the X-ray photoelectron spectroscopy, and the atomic force microscopy indicated that, at such high temperature, implanted In atoms either formed separate phases of metallic In on the SiO₂ film surface or were simply nonexistent due to vaporization.

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1. Introduction

Indium (In) included materials have attracted much attention with regard to chemical catalytic applications [1–7]. For example, an interaction between In and silicon (Si) shows catalytic abilities [1,2]. Recently we have proposed an experimental method [8,9] in which the In implantation into Si containing materials by the ion beam injection was useful for preparing such materials. Yoshimura et al. [8] reported that In implanted silicon dioxide (SiO₂) thin films could catalyze a reaction of benzhydrol with acetylacetone. Our subsequent study [10] also examined whether the catalytic properties depended on the injection energy and/or the fluence of In ions: In ions were injected into SiO₂ films using various ion energies in the range of 50–470 eV and ion fluences in the range of 1×10^{16} – 1×10^{18} ions/cm². It was then found that the catalytic effect was evident only when the ion energy was around 470 eV and the ion fluence was 1×10^{17} ions/cm².

In previous papers on In implantations in Si or SiO₂ substrates [11–15], it has been reported that properties of In implanted substrates depended on substrate temperatures. For examples, Anderson et al. [13] reported that spherical colloids of In were formed on In implanted SiO₂ substrates and the particle size was a function of substrate temperature during implantations. Furthermore, they

reported that optical properties of In implanted SiO₂ were also a function of the substrate temperature. Hence, we have studied here the dependence of the catalytic ability of an In implanted SiO₂ film on the substrate temperature during the ion implantation process. In ions were injected into SiO₂ films using the same ion injection energy (470 eV) and the same ion fluence (1×10^{17} ions/cm²) at different substrate temperatures. In implanted substrate surfaces were analyzed by the X-ray diffraction (XRD), the X-ray photoelectron spectroscopy (XPS), and the atomic force microscopy (AFM). Their catalytic abilities were then examined for the reaction of benzhydrol with acetylacetone, as described before [8].

2. Experimental setup of In ion beam experiment

The In ion beam production experiment was carried out using a low-energy mass-selected ion beam system [16]. The system consists of an ion source, an extractor electrode, a mass selector, a decelerator, and a process chamber, as shown in Fig. 1. The configuration of the modified Freeman-type ion source was shown in Figs. 1 and 2 of Ref. [17]. The procedure of In ion beam production was previously described in [8]. In the ion source, an Ar plasma was generated by a hot tungsten wire and In atoms were sputtered by the plasma from an In₂O₃ target. Among various ions extracted from the ion source, In ions were selected by the magnetic-field based mass selector. In ions were then directed to the process

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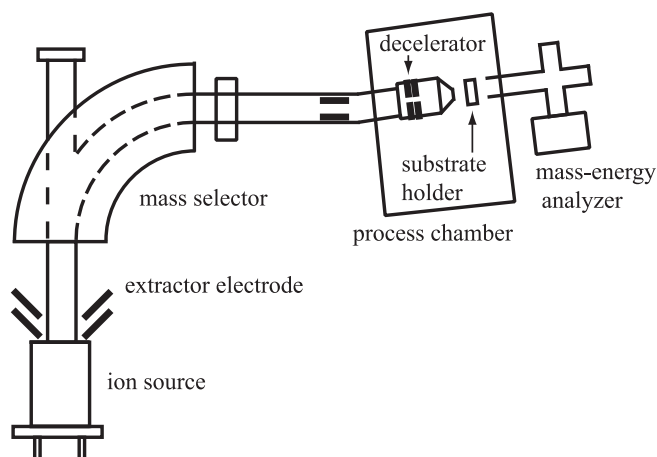


Fig. 1. A schematic diagram of the mass-selected ion beam system.

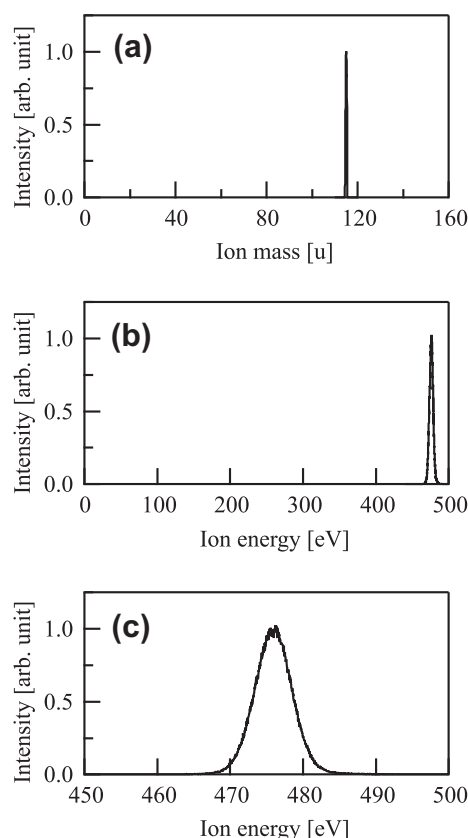


Fig. 2. (a) Mass spectrum of a mass-selected ion beam used in this study. The peak mass number is 115, which corresponds to the mass of In. (b) Energy distribution of the In ion beam used in this study. (c) Enlarged display of the figure (b).

chamber and decelerated by the decelerator. The kinetic energy of In ion beams was 470 eV in the present experiment.

The degree of vacuum in the process chamber was $0.5\text{--}2 \times 10^{-6}$ Pa. In the process chamber, a substrate holder and a mass-energy analyzer (BALZERS, model: PPM421) were installed and either of them was set on the direct path of the ion beam. The mass-energy analyzer PPM421 was placed behind the manipulator on which the substrate holder was mounted (Fig. 1). The substrate holder was connected with an ammeter (KEITHLEY, model: 485) for the ion beam current measurement.

In this study, 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 $0.1\text{ }\mu\text{m}$. The substrate temperature was controlled by a heater set behind the substrate holder and this substrate temperature control system was designed to heat the substrate holder in the range of about $200\text{--}1000\text{ }^\circ\text{C}$. In this experiment, therefore, we were able to assess the dependence of catalytic properties on the temperature only in this particular range. The substrate temperature was monitored by a thermocouple attached to the substrate holder. The temperature monitored by the thermocouple was not identical to the substrate surface temperature, because the thermocouple was not attached to the substrate itself. When the temperature was higher than $400\text{ }^\circ\text{C}$, the temperature of the substrate surface could be measured by a radiation thermometer (CHINO, model: IR-AQ-8CG). The substrate surface temperature was slightly lower than that of the substrate holder. For example, when the thermocouple attached to the substrate holder indicated $790\text{ }^\circ\text{C}$, the substrate surface temperature was $665\text{ }^\circ\text{C}$. We enumerated the temperatures of the substrate holder measured by the thermocouple for convenience.

The present experiment was carried out as follows: samples were prepared with SiO_2/Si substrates and mass and energy selected In ion beams. Then, the sample surfaces were analyzed by XRD (RIGAKU, model: RINT2200), XPS (SHIMADZU, model: ESCA-850), and AFM (JEOL, model: JSTM-4200D). Finally catalytic abilities of the samples were examined.

3. Experimental results and discussion

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 as previously described in [8]. With an appropriate adjustment of the mass selector, we selected In^+ ions as a beam for ion implantation. Fig. 2(a) shows the mass spectrum of such an ion beam measured by PPM421, indicating 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 is shown in Fig. 2(b). Fig. 2(c) shows the enlarged display of Fig. 2(b), indicating that the peak energy is about 476 eV and the full width at half maximum of the peaked profile is about 5 eV. These results show that the In ion beam is nearly monochromatic.

In ion beams were injected into SiO_2/Si substrates. Four In injected SiO_2/Si substrates were prepared at different temperatures [(a) room temperature, (b) $800\text{ }^\circ\text{C}$, (c) $400\text{ }^\circ\text{C}$, and (d) $200\text{ }^\circ\text{C}$] of the substrate holder. The In ion fluences of these four substrates were identical (1×10^{17} ions/ cm^2). The size of each substrate was $1 \times 1\text{ cm}$ and the area exposed to the ion beam was a disk with a diameter of 0.8 cm.

The surfaces of the four In injected SiO_2/Si substrates were analyzed with XRD using $\text{K}\alpha_1$ of Co ($\lambda = 1.78892\text{ }\text{\AA}$) over 2θ range of $32\text{--}47^\circ$. The XRD patterns ($\theta\text{--}2\theta$ method) in Fig. 3(a)–(d) correspond to the above described substrates (a)–(d), respectively. No clear peak is observed in both Fig. 3(a) and (b) whereas peaks corresponding to In are clearly seen in Fig. 3(c) and (d). These results clearly indicate that no metallic In is present on the surfaces of substrates (a) and (b) whereas metallic In exists on the surfaces of both substrates (c) and (d).

To determine whether no In atoms exist on the surfaces of both substrates (a) and (b), we analyzed the surfaces with XPS using $\text{MgK}\alpha$ (12 kV, 30 mA). The XPS spectra in the In 3d region for the substrates (a) and (b) are shown in Fig. 4. Fig. 4(a) shows that two peaks corresponding to In are observed, indicating that In atoms exist on the surface of the substrate (a) without forming a metallic solid phase as seen in Fig. 3(a). An Ar ion beam (600 eV,

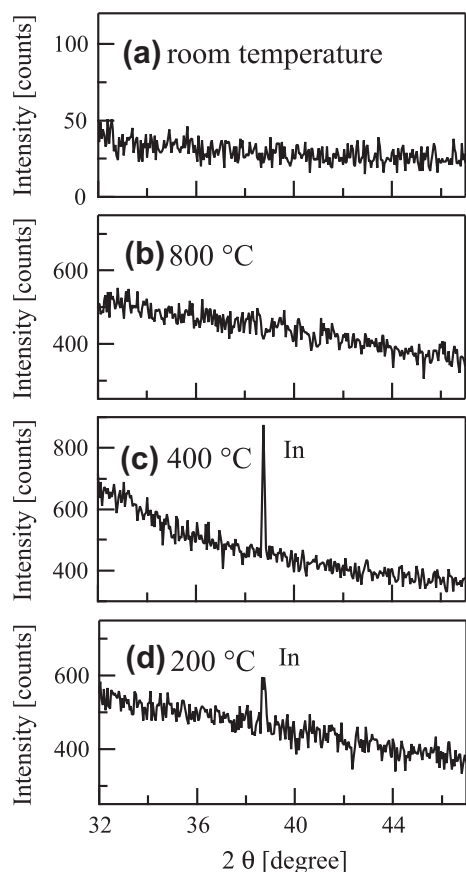


Fig. 3. X-ray diffraction (XRD) spectrum (θ – 2θ method) measured on In injected SiO_2/Si substrate surfaces. The substrate holder temperatures during the injection processes are (a) room temperature, (b) 800 °C, (c) 400 °C, and (d) 200 °C. The In ion energy and ion fluence are 470 eV and 1×10^{17} ions/cm² in all cases.

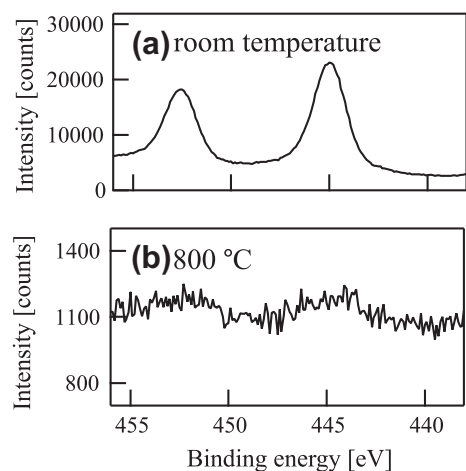


Fig. 4. X-ray photoelectron spectroscopy (XPS) spectrum in the In 3d region for In injected SiO_2/Si substrate surfaces. The substrate holder temperatures during the injection processes are (a) room temperature and (b) 800 °C. The In ion energy and ion fluence are 470 eV and 1×10^{17} ions/cm² in both cases.

50 mA) etching was used to analyze depth profile of In in a substrate which was similar to the substrate (a). It was found that the thickness of In layer implanted was about 10 nm. On the other hand, In peaks are hardly seen in Fig. 4(b), suggesting that nearly no In atoms remained on the surface of the substrate (b).

Atomic-scale morphologies of the surfaces of substrates (a)–(d) were analyzed with AFM, the photographs of which are given in Fig. 5. The data show that the substrate surface morphology depends on the substrate temperature during the In implantation. Fig. 5(b) shows no clear structure, and this is probably due to the absence of In atoms on the surface, as indicated by Figs. 3(b) and 4(b). On the other hand, particle-like structures are seen on the surfaces of other three substrates. The sizes of particle-like structures observed in Fig. 5(c) and (d) are much larger than those in Fig. 5(a). In Fig. 5(c), furthermore, particle-like structures are seen over the entire surface observed by AFM, whereas, large particle-like structures are detected sporadically in Fig. 5(d) and the rest of the surface is covered with smaller structures, as seen in Fig. 5(a). On the basis of the data seen in Fig. 3, we surmise that the large particle-like structures observed in Fig. 5(c) and (d) are metallic phases of In.

The injected In atoms did not exist on the substrate (b) as shown in Fig. 4(b). Therefore, we measured the SiO_2 film thickness change of substrate (b) with a laser interferometer. Indeed, a hollow region due to the etching of SiO_2 film by the In ion injections could be seen on the substrate (b) (data not shown). The number of etched SiO_2 atoms can be calculated based on the volume integration of etched depth and the density of SiO_2 film. Etching yields of SiO_2 film can be obtained from the ratio of the number of etched SiO_2 atoms to that of injected In ions. The etching yield of SiO_2 in this case was evaluated to be 0.15.

Catalytic abilities of the In injected SiO_2/Si substrates were examined based on a reaction that is known to be enhanced by In–Si interactions [18]. The experimental procedure was described elsewhere [10]. Fig. 6 summarizes the reaction results obtained from the respective substrates (a)–(d) mentioned above. The percentage shown here is the molar distribution. In Fig. 6, the reaction of benzhydrol (1) and acetylacetone (2) produces the coupling product (3) and bis(diphenylmethyl) ether (4). In the case (a) (room temperature substrate), the yields of the coupling product and bis(diphenylmethyl) ether were 6% and 38% respectively, clearly indicating the presence of catalyzing effect of the In implanted SiO_2/Si substrate [10]. The chemical reaction occurred on the surface of In. The hydroxyl group of benzhydrol (1) coordinates to In atoms on the surface, inducing the corresponding carbocation and hydroxide anion. Then, the carbocation reacts with acetylacetone (2) and benzhydrol (1), resulting in the production of the coupling product (3) and bis(diphenylmethyl) ether (4), respectively. When the substrate holder temperatures during the In injections were (b) 800 °C, (c) 400 °C, and (d) 200 °C, the yields of the coupling product and bis(diphenylmethyl) ether were null, and nearly 100% of benzhydrol was recovered. These results suggest that the catalytic effect depends on the substrate temperature during the In injections. In separate experiments, we have confirmed that either metallic solid In alone or SiO_2/Si substrate alone does not catalyze the reaction [8].

The XPS spectrum of the substrate (a) (Fig. 4(a)) indicates an energy shift from metal In peak. This energy shift is indicative of the presence of a +3 valence In compound formed on the surface of the substrate (a). Generally, In metal does not work as a Lewis acid catalyst. On the other hand, In(III) has Lewis acidity to show catalytic activity. Therefore, the result observed in Fig. 4(a) does not conflict with the catalytic activities of In injected SiO_2/Si substrate (Fig. 6(a)).

In the process chamber at a gas pressure of $0.5\text{--}2 \times 10^{-6}$ Pa, the melting and boiling temperatures of In are about 160 and 450 °C, respectively. As discussed earlier with the XRD (Fig. 3(b)) and the XPS (Fig. 4(b)) results concerning the substrate (b), it is conceivable that nearly no In atoms remained on the substrate, since the substrate holder temperature was much higher than the boiling temperature. This explains the observation of Fig. 6(b) where no catalytic reaction actually occurred. In the substrates (c) and (d),

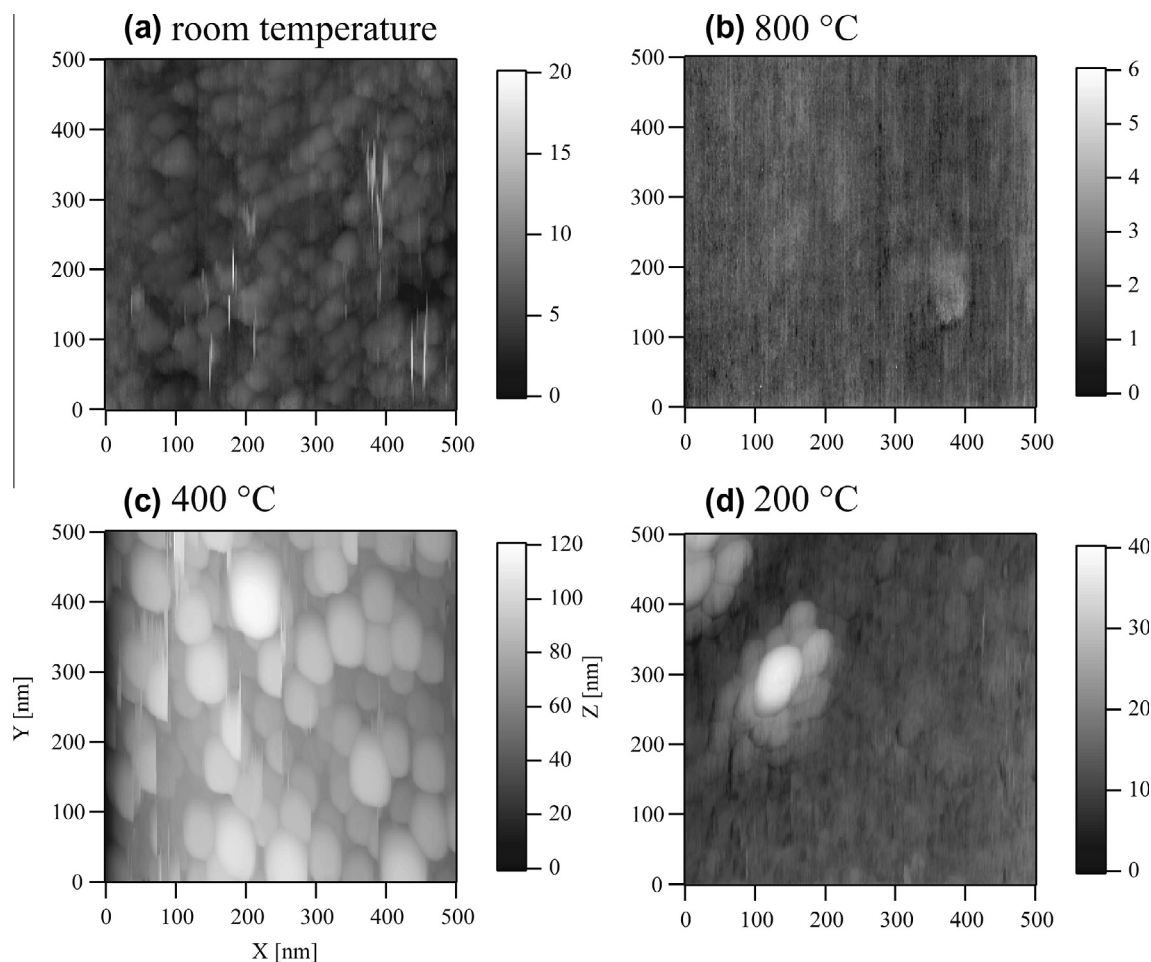


Fig. 5. Atomic force microscopy (AFM) images of In injected SiO₂/Si substrate surfaces. The gray scale on each figure indicates the height in units of nm. The substrate holder temperatures during the injection processes are (a) room temperature, (b) 800 °C, (c) 400 °C, and (d) 200 °C. The In ion energy and ion fluence are 470 eV and 1×10^{17} ions/cm² in all cases.

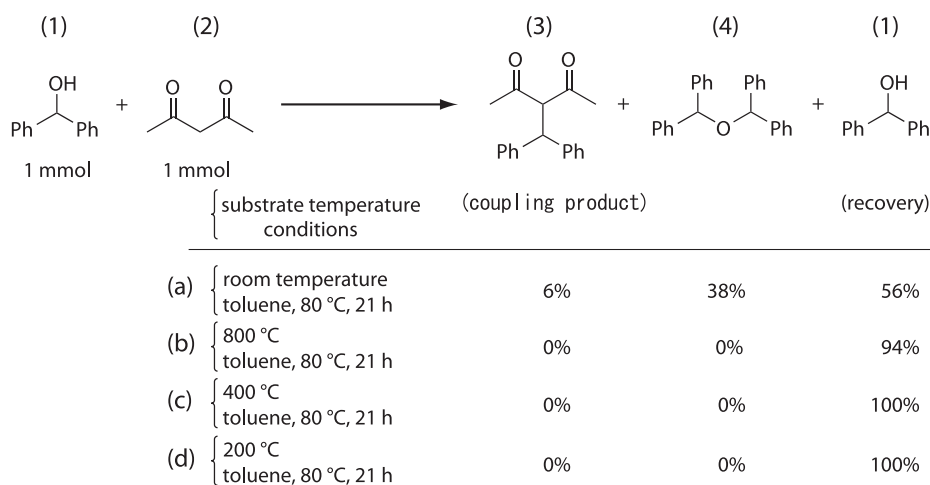


Fig. 6. Yields of the benzhydrol and acetylacetone reactions using In implanted SiO₂/Si substrate catalysts under different conditions.

the substrate holder temperatures were between the melting and boiling temperatures. As shown by the XRD results (Fig. 3(c) and (d)), metallic In surface layers were formed on the substrates, indicating that the number of In atoms dispersed on the top of SiO₂ surface layer was insufficient.

4. Summary and conclusions

We have used In ion beam injection into a SiO₂ thin film to create a material that has both In and Si in close proximity, which exhibits a catalytic effect on an organic chemical reaction. Our

study indicated that the catalytic effect of In injected SiO₂ thin films strongly depends on the substrate temperature during the In injection process.

The In ion beams were produced in the mass-selected ion beam system with an ion energy of 470 eV and an ion fluence of 1×10^{17} ions/cm² and injected into SiO₂/Si substrates at different substrate temperatures. The substrate surfaces were then examined by XRD, XPS, and AFM. When the sample was prepared at room temperature during the injection process, it acquired an ability to catalyze the benzhydrol–acetylacetone reaction. When In ions were implanted into a SiO₂ film at the substrate holder temperature of 200 °C or higher, no catalytic effect was observed. This is probably due to the fact that, at such high temperatures, injected In atoms either become metallic solid phase on the substrate or can not remain in the substrate because of vaporization. It seems likely that the highest substrate temperature which allows to induce the catalytic ability depends on the In ion injection energy, ion fluence, and ion flux, because the beam energy can increase the surface temperature at atomic scale and thus enhance the transport of In atoms. A further study is necessary to determine the allowable substrate temperature for the formation of In implanted SiO₂/Si substrates.

In practical applications, In–Si based catalytic surfaces must be produced in a cost effective manner and obviously the use of ion beams would not be the first choice for mass production of such materials. A plasma process may be used for providing energetic In ions to a SiO₂ surface of large area at relatively low cost. For example, ionized magnetron sputter deposition [19,20] is a plasma-based method to generate nearly unidirectional metal ions whose impinging energy can be controlled by the applied bias voltage to the substrate surface. In the ionized magnetron sputter deposition process, metal ions are produced from a metal target by an Ar plasma generated by a magnetron system placed on the back side of the target, as in the ordinary magnetron sputter deposition process. Sputtered metal atoms are then ionized by another plasma separately generated in the magnetron sputter deposition system and accelerated by the bias voltage toward the substrate surface. Since metal atoms typically have ionization energies much lower than that of Ar (e.g., the ionization energy of In is 5.8 eV),

sputtered metal atoms are fully ionized by an Ar plasma in general. We believe that the ionized magnetron sputter deposition process could be used cost-effectively for the commercial production of In–Si catalytic surfaces discussed in this article.

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