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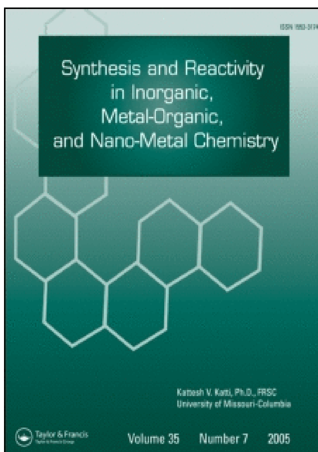

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Iron Oxide Thin Film Deposition on Si(100) Substrate using MOCVD Method

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Iron Oxide Thin Film Deposition on Si(100) Substrate using MOCVD Method

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We have deposited iron oxide thin films on Si(100) substrates using single molecular precursor in the range of 300–500°C by metal-organic chemical vapor deposition (MOCVD) method. Iron pentacarbonyl [$Fe(CO)_5$] and oxygen gas were used as the iron source and oxidizing agent, respectively. The Si(100) wafer was used a substrate and it was cleaned by sequential ultrasonic baths of acetone, ethanol, HF (10%) and rinsed by de-ionized water. To deposit the iron oxide thin films on the substrate, O_2 reactive gas was needed during the deposition. We have studied the changes of morphology, crystallinity and thickness of films deposited at various ratios of injected precursor to O_2 volume as well as several deposition temperatures. The as-grown thin film was first characterized by X-ray diffraction (XRD) for the study of crystallinity. To confirm the morphologies and thickness, scanning electron microscopy (SEM) analysis was also performed. To identify the composition of the deposited thin films, energy dispersive X-ray (EDX) and X-ray photoelectron spectrometry (XPS) analyses were carried out.

Keywords iron oxide, iron pentacarbonyl, MOCVD

INTRODUCTION

Recently, metal oxides have been used extending to wide industry for their optical, electrical, chemical and physical properties.[1,2] Specially, iron is synthesized and studied a pure and/or mixed oxide form because their chemical and physical properties are depending on their chemical composition and crystal structure.[3] Iron complexes consisted of iron and oxygen, such as FeO, α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4, are used in various parts with different properties, and each other, so it is important to control them for each application.[4]

For growth of iron oxide thin films, there are several methods that are physical (sputtering, molecular beam epitaxy [MBE], RF) and chemical ways (chemical vapor deposition [CVD], solgel, chemical solution). Among them, metal-organic CVD (MOCVD) method is a technique for depositing thin layers of atoms onto substrate.[5] The great advantage of metal-organic precursor is their generally high volatility at moderately low temperature. It is easy to modulate not only thickness, but also various functional multi-layers on substrate since the control of gas flow rates and partial pressure is possible without dealing with troublesome liquid or solid source in a reactor at low deposition temperatures.[6]

As precursor of iron oxide, there are some representatively materials such as iron pentacarbonyl[$Fe(CO)_5$], iron trichloride ($FeCl_3 \cdot 6H_2O$), iron tert- butoxide[$Fe(O^tBu)_3]_2$, iron acetylacetonate[$Fe(acac)_3$] and ferrocene dissolved isopropyl.[5] Because iron oxide has magnetic properties and is chief, it is actively studied for using recording media and gas devices.[3,7] In medical parts, it is acted as a target material of drug delivery system using magnetic properties.[8]

In this work, we have deposited iron oxide thin films on Si(100) substrates using iron pentarcarbonyl and O_2(99.999%) as precursor and reactive gas by MOCVD method. For study of iron oxide thin films deposited on Si(100) substrate, we have deposited them at various deposition temperature and partial pressure between precursor[$Fe(CO)_5$] and reactive gas (O_2).

EXPERIMENTAL

Thin films of iron oxide were deposited via a home-made horizontal metal-organic chemical vapor deposition (MOCVD) technique under 2×10^{-2} Torr. We used a iron pentacarbonyl as a precursor purchased from Sigma–Aldrichas (CAS: 13463-40-6). It is dissociated iron and carbon monoxides:[6]

$$Fe(CO)_5 \rightarrow Fe + 5CO$$

For oxidation of iron dissociated from precursor, we poured high purity oxygen gas into the chamber. Moreover, since iron pentacarbonyl has a high vapor pressure in room temperature (35.25 Torr at 25°C), the deposition was carried out without precursor bottle heating.

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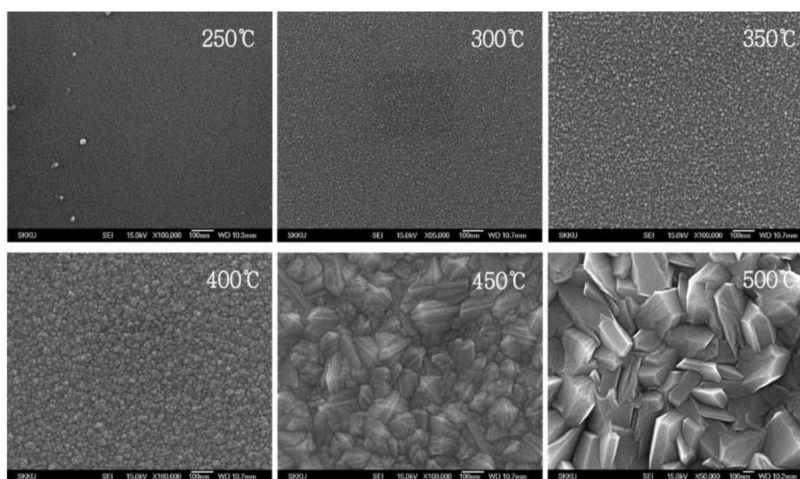

FIG. 1. Scanning electron microscopy views of films deposited for 1 hour at various substrate temperature (fixed precursor partial pressure ratio; precursor/Oxygen = 15 mTorr/20 mTorr).

A p-type Si(100), typically $1.5 \times 2\ cm^2$, was rinsed in acetone, HF(10%) and deionized (DI) water before deposition to remove dust and organic impurities. We carried out deposition of films at a various deposition temperature in a range of 200–500°C by thermal heating because deposition temperature is one of the most important factors to surface modification in CVD technology.[6] To confirm the effect of partial pressure of both precursor and oxygen gas during deposition, we also mixed both gas to various ratios. The deposited films were analyzed with scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX), X-ray photoelectron spectrometry (XPS) and micro–Raman spectroscopy (with 514 cm^1 lazer).

RESULTS

Figure 1 shows the SEM images of deposited iron oxide thin films on Si(100) substrates at diverse temperature. All films were deposited at 2×10^{-2} Torr of precursor: oxygen = 15:20 condition. The deposited films were able to observe over 300°C about 10 nm by electric equipment. As rising growth temperature, the thickness of deposited thin films was significantly increased while the grain size is getting bigger from 7 nm to 15 nm. Over 400°C, the particles were rapidly aggregated on the surface each other by thermal energy effect. We also confirmed the growth rate of deposited film by measuring of thickness observed in cross-sectional SEM images.

Figure 2 shows the growth rate of deposited films on Si(100) substrate per minute. At 250–400°C, the growth rate is gently increased about 1–2 nm/min. However, the thickness was suddenly increased about 5 nm/min. over 400°C. We have also studied film properties about deposition time, but films were not influence on crystallity and structure of films except for changing of thickness. Therefore, we chose the deposition condition of 350°C. At this deposition temperature, it was possible to deposit a uniform, high quality and controllable film. The partial pressure of precursor and oxygen was changed over from 1:1 to other ratio ((a) 1:1.67, (b) 1:1.5, (c) 1:33, (d) 1:0.6 and (e) 1:0.5) for 1 hour at 350°C. Figure 3 (a) shows the XRD data of iron oxide films deposited with various partial pressure mixed iron and oxygen. The iron oxide thin films were deposited with mainly magnetite (Fe_3O_4) structure on the Si(100) substrate at 350°C.[3,9,10] Peculiarly, the hematite structure was found at 39.2° when the partial pressure ratio of deposited films is between around 0.4 to 0.6 ratio. Maybe there is a limited ratio between iron and oxygen to growth hematite structure. That is around from 0.4 to 0.6 rate in our experiment data. The changing of growth rate shows in Figure 3(b) according to the difference of partial pressure. The thickness of iron oxide thin films was rapidly increased and colorchanged from blue and yellow to dark gray as increasing of O_2 ratio. In Figure 3(b) region I,

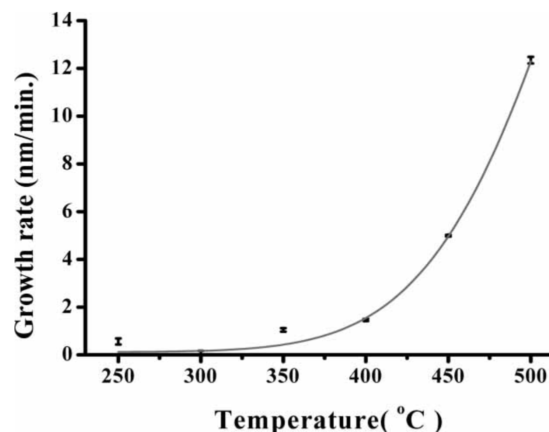

FIG. 2. The growth rate of deposited films with different deposition temperature.

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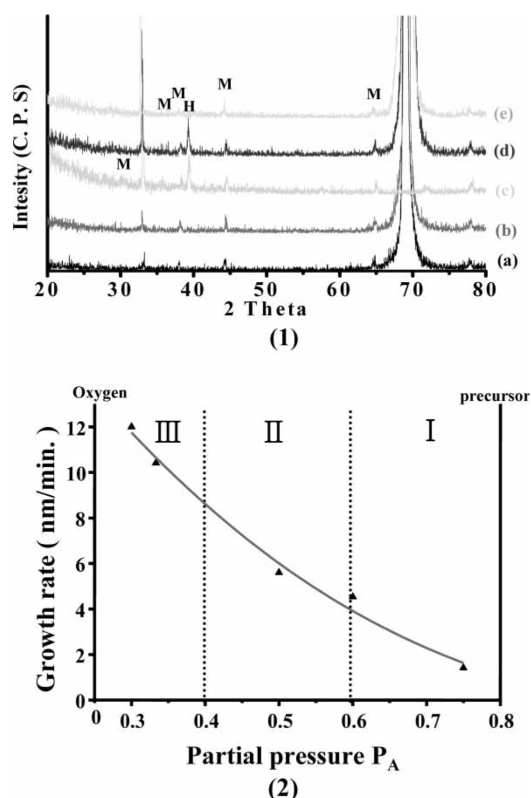

FIG. 3. (1). Room temperature XRD patterns of iron oxide films with different mole faction of precursor: (a) 0.375, (b) 0.4, (c) 0.42, (d) 0.6 and (e) 0.67; M: magnetite (Fe_3O_4); H: hematite (α-Fe_2O_3). (2). The growth rate of iron oxide thin films depositied on Si(100) at 350 °C with various mole fraction of reactant gas.

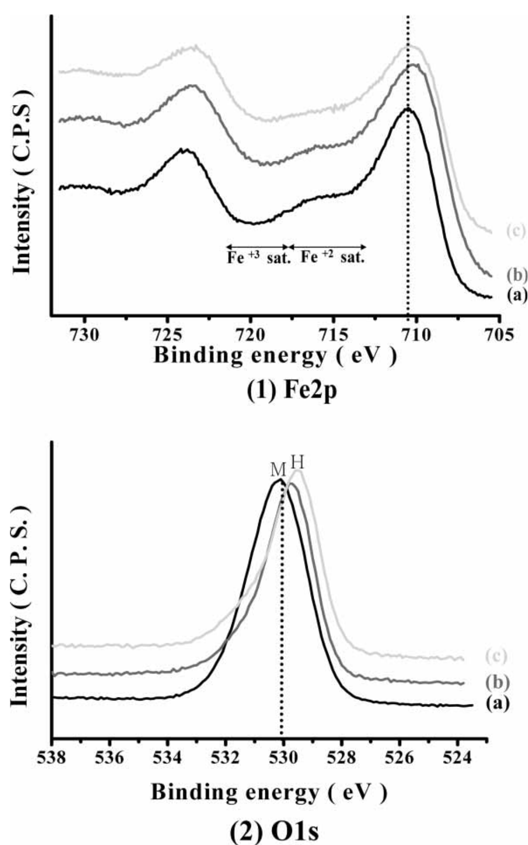

FIG. 4. XPS spectra of iron oxide deposited on Si(100) substrate at 350 °C with different precursor ratio. XPS (1) (2) high-resolution XP spectrum of Fe2p and O1s: (a) 0.4, (b) 0.57 and (c) 0.66; M: magnetite (Fe_3O_4); H: hematite (α-Fe_2O_3).

as partial pressure of oxygen increases the quantity by three times than precursor, the films, easily took off from the substrate. This reason is thought that the deposited film including reach oxygen react with native oxide and water of surface of substrate by thermal energy or the sudden oxidation of iron, make worse adhesion between thin film and substrate. In region III, we have observed the changes decreasing in thickness at low partial pressure of oxygen. However in region II; there were two phases, magnetite and hematite. Therefore, it was possible to control the thickness of iron oxide thin films by modulation of concentration of reactive gas.

The atomic compositions of the deposited films were analyzed by XPS. Figure 4 shows XPS spectra of deposited iron oxide thin films deposited at 350°C with different concentrations of reactive gas. The partial pressure ratio of precursor is 0.4, 0.57 and 0.66, respectively. All the deposited iron oxide thin films were included strong Fe and O peaks and a little C peak. The carbon was almost removed after Ar ion bombardment for 10 min. Figures 4(a) and (b) show the high-resolution XPS spectra of Fe 2p and O 1s after Ar ion bombardment, respectively. The Fe 2p core levels were split into $2p_{1/2}$ and $2p_{3/2}$ components. In Figure 4(a), each Fe 2p spectrum shifted to low binding energy and Fe $2p_{3/2}$ peak was broader than that of a free Fe (707 eV) atom as increasing of precursor partial pressure. This is why iron of magnetite consists of both Fe^{3+} (711 eV) and Fe^{2+} (710 eV) species.[11] Because the satellites of the Fe 2p core levels can give a much better indication of oxidation state than binding energy alone, we compared the satellite peak of Fe^{2+} and Fe^{3+}. In more reach oxygen condition, the satellite peaks showed the amount of Fe^{3+} is more increased than Fe^{2+}, which is in a good agreement with XRD data and O 1s result. The O 1s peak was shifted from position of magnetite (530.3 eV) to hematite (529.6 eV), too.[1,4,12]

The clear and convincing evidence of deposition film was measured by micro-Raman analysis with a 514 nm laser and 20 mW power at room temperature. The Raman analysis had been carried out to confirm the stretching mode and component of deposited films. The Raman active band in magnetite and hematite crystals are clearly observed at 669 and 427 cm^{-1}, respectively. As concentration of iron increased, the intensity of magnetite peak was decreased not only the bonding of magnetite (300 cm^{-1}), but also the stretching mode (670 cm^{-1}); hence the intensity of hematite band was increased.[13–16] That reason is as the amount of magnetite is decreased, the amount of

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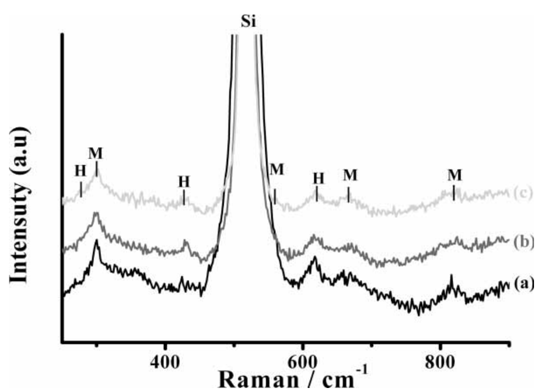

FIG. 5. The micro-Raman spectra(with 514 nm laser) of deposited films at 350°C: the rate of precursor and oxygen is (a) 0.23, (b) 0.4 and (c) 0.57; M: magnetite (Fe_3O_4); H: hematite (α-Fe_2O_3).

hematite was increased. Therefore, the micro-Raman spectra well agreed to the previous mention (Figure 5).

CONCLUSION

We have deposited the iron oxide films on Si(100) substrate using MOCVD method with iron pentacarbonyl and high pure oxygen. We have studied the effects of deposition temperature, time and partial pressure of mixed reactive gas to growth thin film. The deposited grains are aggregated to each other, and the change of thickness is rapidly increased at over 400°C. Though XRD measurement, the concentration of mixed reactive gas affects the structure of iron thin films. Additionally, the study of structure and components is performed using XPS and micro-Raman equipment. This study has shown that it was possible to control the structure and thickness of deposited iron oxide thin films with good morphology.

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