Effect of Assisted Ion Energy on Properties of Silicon Oxide Thin Film Deposited by Dual Ion-Beam Sputtering

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ABSTRACT: A silicon oxide thin film barrier was prepared with different oxygen ion energies, and its chemical composition, surface morphology, optical, and barrier property related to the deposition condition were characterized and discussed. Our study showed that in O_2-assisted process the stoichiometric silicon oxide thin film was obtained at a critical deposition condition of 100 eV oxygen ion energy. The thin film deposited at the critical condition showed the lowest surface roughness giving similar or higher optical transmittance than that of pure polycarbonate substrate. The boiling and tensile tests performed on the thin film deposited using assisted ions prior to the deposition process showed improvement in the adhesion between the oxide barrier layer and the polymer substrate. In addition, interface domination for improving the barrier properties of silicon oxide thin film was achieved through introduction of dual ion-beam sputtering without pretreatment. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2444–2452, 2007

Key words: silicon oxide thin film; oxygen ion energy; O_2 assisted; adhesion improvement; barrier properties

INTRODUCTION

Recently, new deposition techniques have been devised to obtain oxide barrier layer with oxygen permeability lower than that which can be measured by oxygen transmission rate (OTR) analysis.[1] To obtain such a barrier layer, three different parts of the thin film including surface, bulk, and thin film/substrate interface need to be optimized. The surface properties affecting the barrier property such as roughness, porosity, scratch, erosion, and corrosion resistance must be effectively controlled. The thin film barrier layer also needs to have a stoichiometric composition giving an optical refractive index similar to that of bulk. Furthermore, thin film-substrate interfacial bonding and adhesion need to be enhanced, but residual stress should be minimized. Finally, the polymer substrate property needs to be well matched to that of the barrier layer being deposited.[2]

By utilizing the characteristics of the dual ion-beam sputtering, the desired barrier layer properties can be achieved through effective control of process parameters.[3,4] In dual ion-beam sputtering, chemical bonding can be improved by increasing the collision between ions or atoms through energy supplied by the ion bombardment. In addition, RF plasma effect can be separated from the sample and can confine ion beams between the target and the sample.[5,6] Therefore, dual ion-beam sputtering with an assisted ion gun can improve the thin film adhesion, density, stoichiometry, and optical transmittance at short wavelength.

Since the formation of columnar and micro-porous structure, poor stoichiometry, low density, and adhesion deters synthesis of high quality thin film,[7–9] ion bombardment was applied during deposition to surmount such adverse effects.[10–13] In addition, ion bombardment using reactive gas like O^{+}/O^{2+} can improve the stoichiometry of the deposited oxide thin film and enables the control of the properties related to it. Low energy reactive ion beam (inert, reactive, or mixed ion) bombardment can also increase the rate of compound formation, control the stoichiometry, and improve adhesion of deposited thin film.[14–16] Ion bombardments enhance adhesion by producing adhesion sites on the surface, which influence both stoichiometry and optical property of the oxide thin film deposited.[17,18] Therefore, our study is mainly concentrated on observing the surface, bulk, and the interfacial properties related to the assisted ion energy as a deposition parameter for improving the barrier layer properties. In addition, improvement in surface property of the oxide thin film deposited by an ion-beam assisted process similar to that with pretreated deposition process have been investigated.

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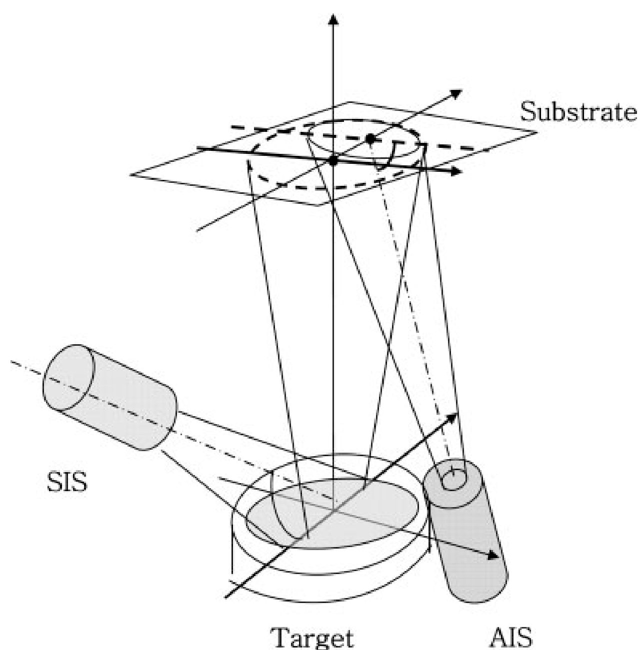


Figure 1 The schematic diagram of dual ion-beam deposition (DIBD).

EXPERIMENTAL PROCEDURE

Chamber equipment and deposition

Two cold hollow cathode-type ion guns were attached to the deposition chamber. One of the ion guns generates particle flux from the solid sputtering target, whereas the other assists the thin film growth by generating various inert or reactive ions. The incident angle of the ion beam used for sputtering the solid target was 50° and the assisted ion-beam source (AIS) was generated by a cold hollow cathode ion source attached to the target holder inside the vacuum chamber. The assisted ion gun is placed at the axis of the thickest point of the deposited thin film with incident angle of 40°. Figure 1 shows the schematic diagram of a dual ion-beam deposition setup. Due to the AIS ion-beam current distribution, the homogeneous thin film deposition area is reduced to a circular region of ~ 30 mm in diameter. A movable Faraday cup was used to control the ion-beam current at the center of the target. Rotary and turbo molecular pumps were used for vacuum systems where a pirana and ion gauge were used to measure low vacuum level (~ 10^{-2} Torr) and high vacuum level (~ 10^{-6} Torr), respectively. The *in situ* deposition rate control was possible by placing a quartz crystal oscillator near the substrate.

An ion-assisted process including O_2-assisted process was applied to obtain silicon oxide thin film using a silicon (diameter: 150 mm, thickness: 6 mm, purity: 99.999% (5*N*); High Purity Chemical, Japan) target with 1 keV Ar ion bombardment. To control and maintain the deposition condition, the total current and density of SIS was measured using a Faraday cup,

TABLE I
The Deposition Condition Parameters of Silicon Oxide Thin Films by O_2-Assisted Ion Sputtering

Assisted ion source parameters (AIS : O_2)	Values
Gas (AIS used)	Oxygen (purity: 99.99%)
Ion energy	0–400 eV
Ion beam current	0–22 mA
Discharge voltage	500 V
Oxygen pressure	4.5×10^{-4} Torr
Incident angle to target	40
Base pressure	5×10^{-6} Torr

whereas the deposition rate and thickness was controlled using a quartz oscillator. For ion-assisted bombardment, oxygen (O^+ and O^{2+}) was used. The base pressure of the deposition chamber was 5×10^{-6} Torr, but when SIS and AIS was applied, the pressure was 2×10^{-4} Torr and 4×10^{-4} Torr, respectively. The surface oxide layer on the target was removed by Ar ion bombardment at 400 eV for 20 min. Both polycarbonate (PC) and silicon wafers were used as substrates for different analyses. The silicon oxide thin film deposited on the PC substrate was used for characterizing chemical composition [XPS and Fourier transformed infrared (FTIR)], surface roughness, structure, optical property, and oxygen permeability, whereas a silicon substrate was used for refractive index, deposition rate,

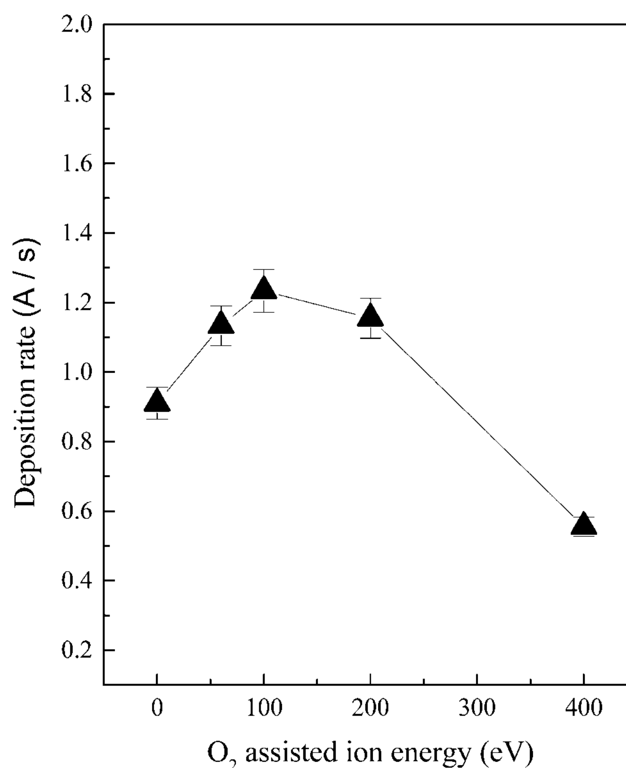


Figure 2 Changes in deposition rate of silicon oxide thin film prepared by O_2-assisted sputtering method with oxygen ion energy.

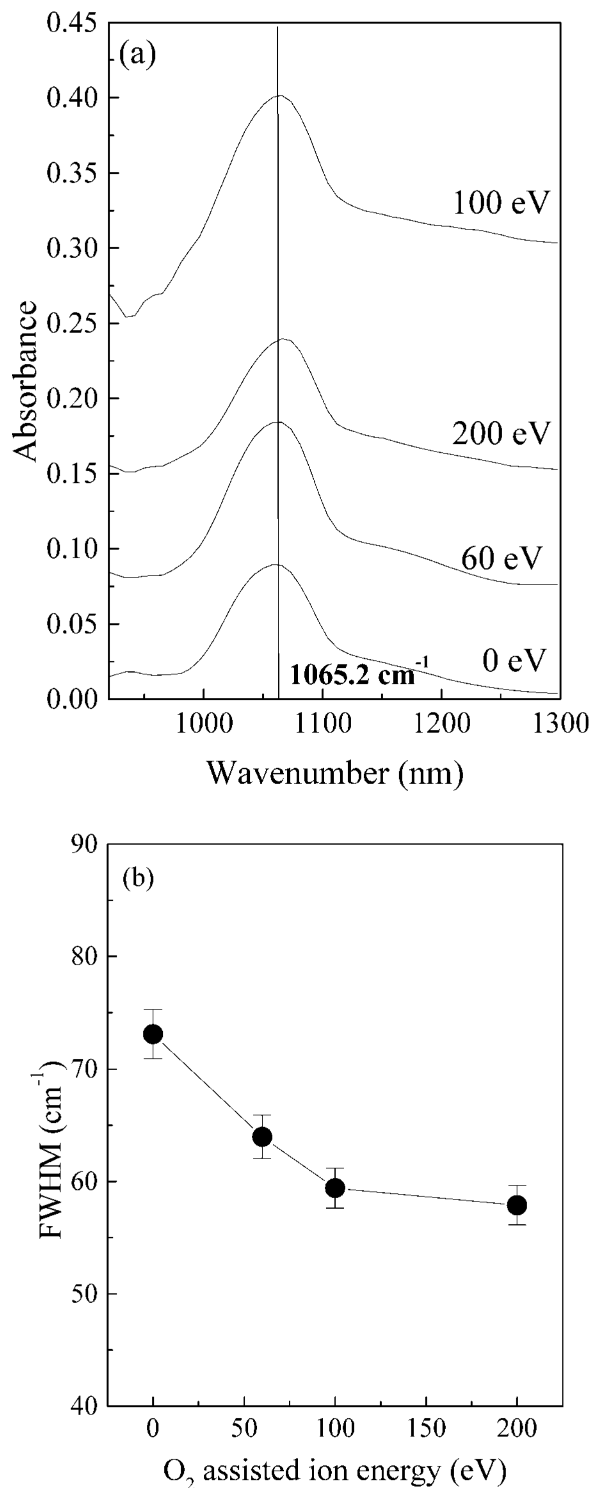


Figure 3 Dependence of the IR spectrum (a) and the full width at half maximum (FWHM) (b) for the Si—O—Si stretching mode on the oxygen ion energy prepared by O_2-assisted sputtering.

and thickness measurement. The 185-μm-thick PC substrate was first cleaned with alcohol after removing the cover film to prevent electrostatic charge built up and then blown dried using N_2 gas to prevent scratching of the surface. The *p*-type silicon wafer substrate was cleaned by immersing in HF solution to remove the native surface oxide layer, followed by sonicating in acetone and deionized water for 15 min each. SIS total ion-

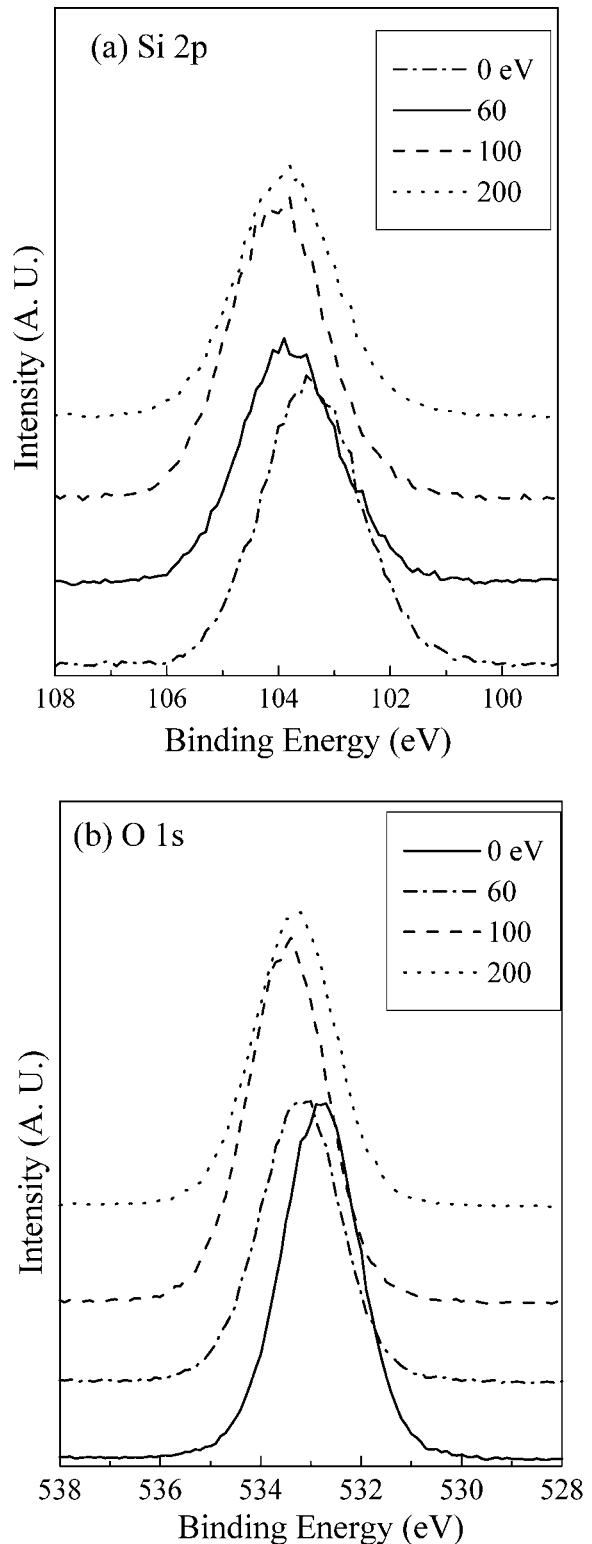


Figure 4 XPS spectra of (a) Si 2p and (b) O 1s core levels of silicon oxide thin film deposited by O_2-assisted sputtering as a function of oxygen ion energy.

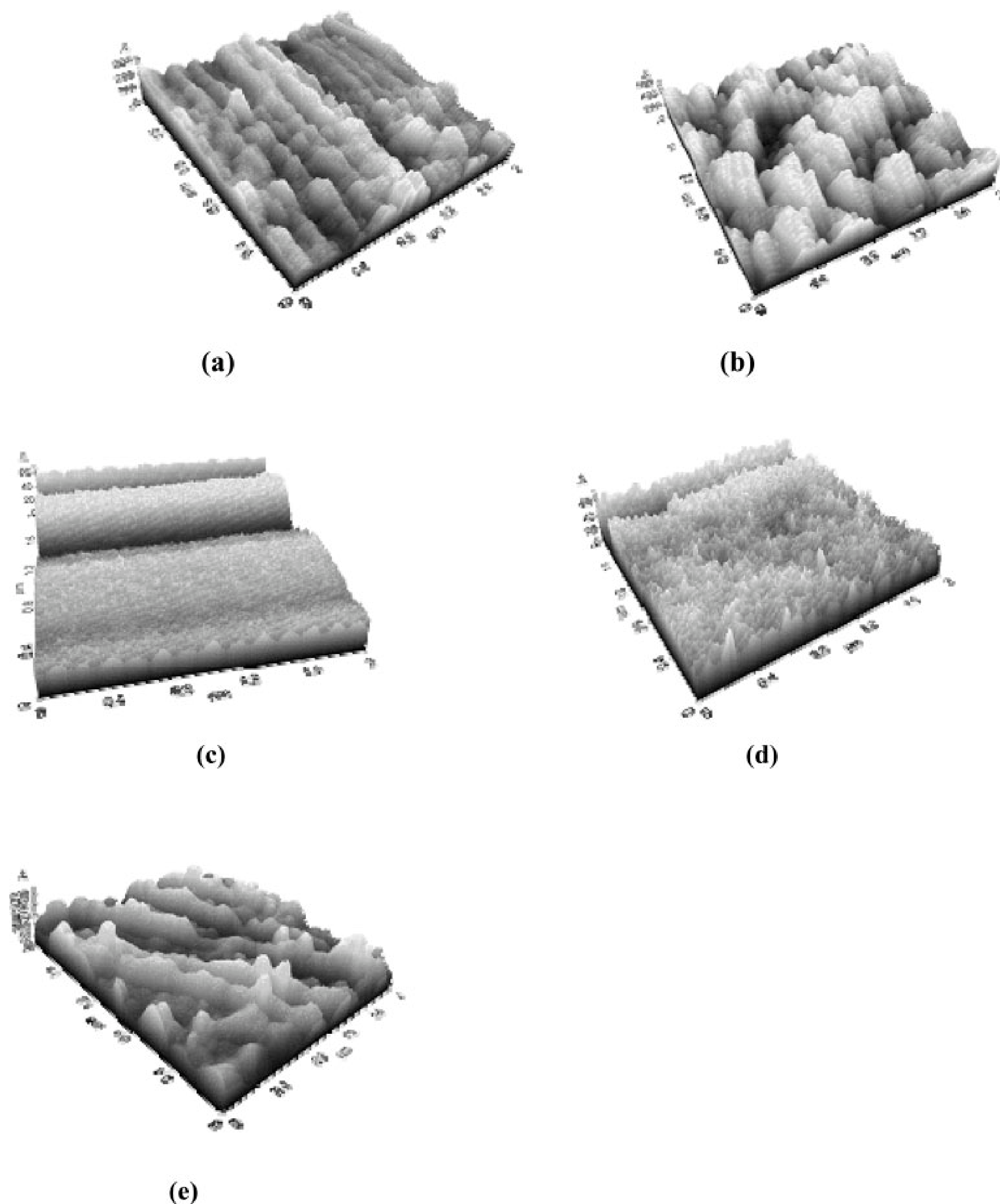


Figure 5 AFM 3D images of silicon oxide thin film on PC substrate prepared by O_2-assisted sputtering with varying oxygen ion energy: (a) 0 eV, (b) 60 eV, (c) 100 eV, (d) 200 eV, and (e) 400 eV.

beam current was 35 mA with current density of 1 mA/cm^2. The experimental parameters for the O_2-assisted processes are summarized in Table I.

Analyses and measurements

To control the deposition rate, the thickness of the thin film deposited for equal period of time through O_2-assisted process was measured from the cross-sectional image obtained by scanning electron microscope (SEM; *S*-4200FE; Hitachi, Japan). To analyze the silicon oxide thin film stoichiometry, FTIR spectroscopy (Perkin–Elmer, OH, model: 580) was used to measure the shift in absorption peak between 800 and 1300 nm. The error range of stoichiometry analysis was less than 4%. How-

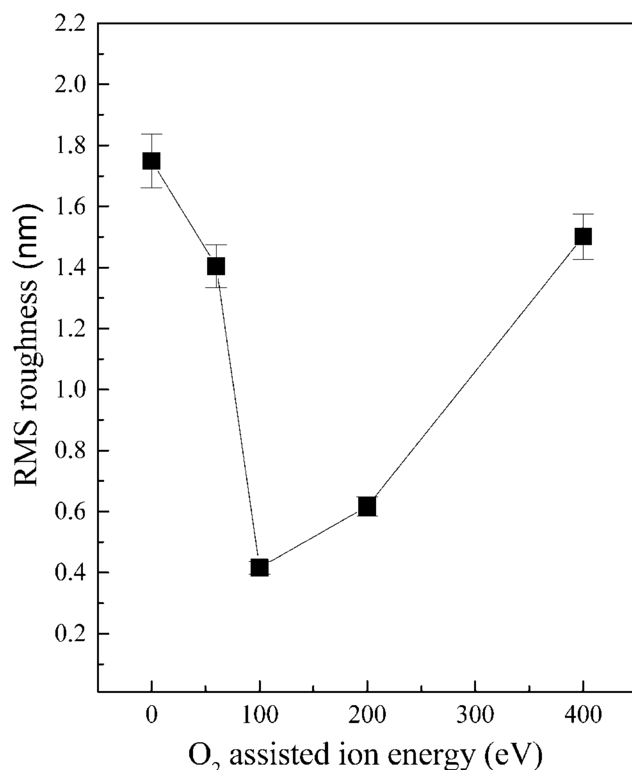


Figure 6 Root mean square roughness of silicon oxide thin film on PC substrate deposited by O_2-assisted sputtering as a function of oxygen ion energy.

ever, the possible presence of trace amounts of impurities cannot be completely ruled out. The optical transmittance of the deposited thin films were measured by using UV–Vis spectrophotometer (model: HP 8452; Hewlett–Packard, USA) between 300 and $\sim$ 800 nm wavelength and the refractive index at 560 nm was measured by ellipsometry. Surface morphology and roughness were characterized after scanning 2 μm × 2 μm area of the deposited thin film by atomic force microscopy (AFM; SFM-BD2; Park Scientific Instruments, USA). OTR of the oxide thin film barrier was measured using Oxtran instrument (2/60; MOCON) at 30°C with 0% relative humidity. Since the OTR dependence on the thickness of the silicon oxide thin film is well known, thin film thickness was fixed to a thickness with minimum OTR called critical thickness to neglect the thickness effect. Since the 300 Å thin film showed the lowest OTR, the thickness was fixed to 300 Å irrespective of the parameter condition applied. When thickness of the deposited film was larger than critical thickness, OTR decreased due to stress relief cracking.[19]

RESULTS AND DISCUSSION

Processing parameter and composition analysis

Deposition rate is one of the most critical process parameter that governs the characteristics of oxide thin film when element target is being used. Therefore, the deposition rate dependence on the assisted ion energy is shown in Figure 2. As the assisted ion energy is increased to 100 eV, the deposition rate also increased from 0.9 A/s to 1.2 A/s but decreased to 0.5 A/s

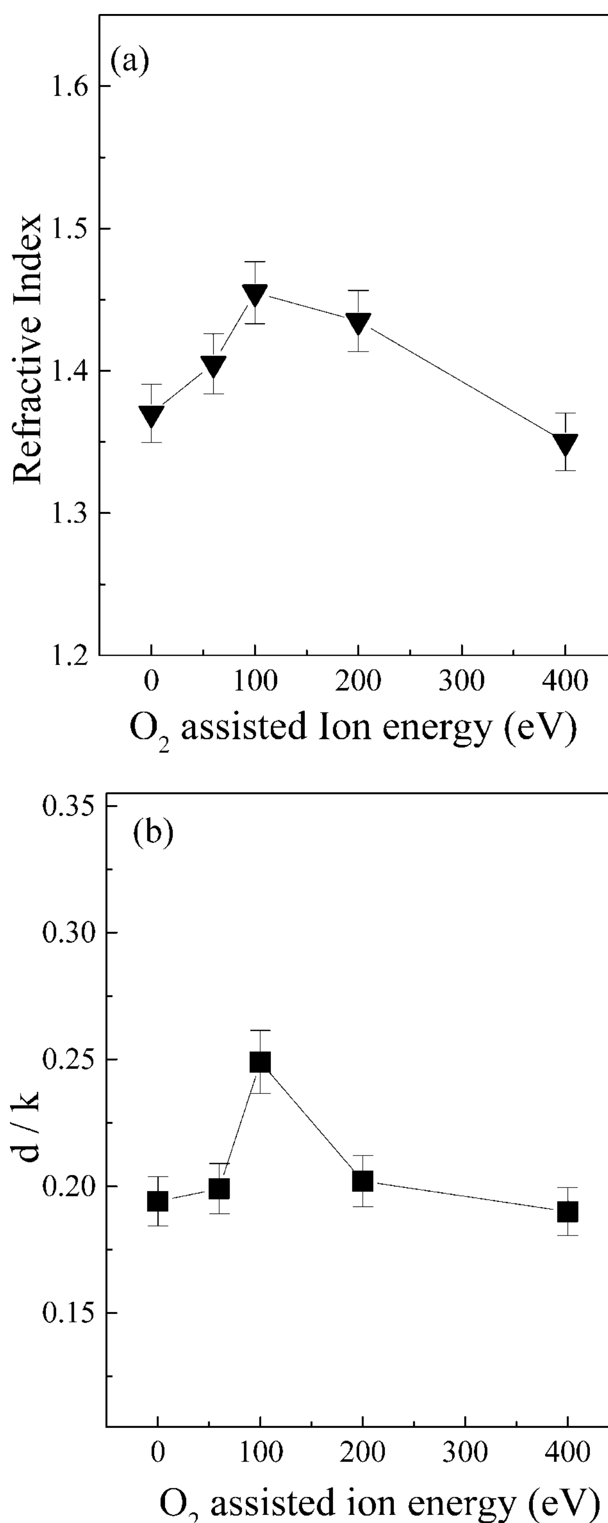


Figure 7 (a) Refractive index and (b) relative density of silicon oxide thin film on Si substrate deposited by O_2-assisted sputtering as a function of oxygen ion energy.

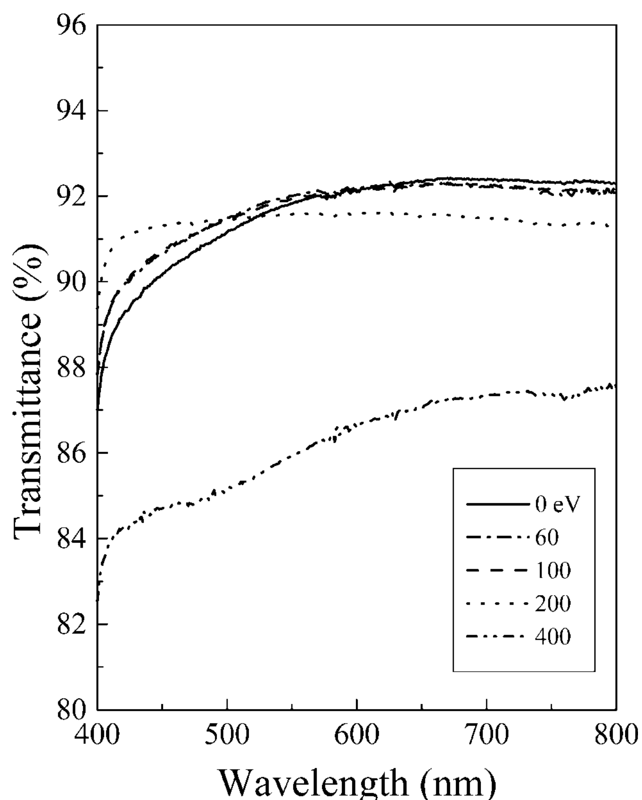


Figure 8 Change of optical transmittance of silicon oxide thin film on PC substrate prepared by O_2-assisted sputtering according to oxygen ion energy.

when ion energy was further increased. The increase in deposition rate between 60 and 100 eV is due to easier atomic bonding, to form a new compound through densification, as the mean free path of the oxygen ions with constant kinetic energy is increased. However, when ion energy is supplied above certain level, deposition rate decreases due to the surface etching caused by resputtering effect rather than formation of chemical bonding by irradiation.[20] The chemical bonding nature of the SiO_2 thin film obtained through O_2-assisted process was characterized by FTIR analysis shown in Figure 3(a). The IR absorption peak near 1060–1065 cm^{-1} related to the Si—O stretching mode appeared for the sample obtained with assisted ion energy in the range of 0–200 eV, indicating that homogeneous and nearly stoichiometric silicon oxide thin film has been formed. Figure 3(b) shows the full-width at half-maximum (FWHM) related to the O_2-assisted ion energy where the FWHM decreased with increase in the assisted ion energy. Figure 4(a) shows the Si 2p core level of silicon oxide thin film deposited with different assisted ion energies.

As can be seen in the Figure 4, when applied assisted ion energy was in between 0 and 200 eV, Si 2p peak near 103.5–104 eV appeared related to Si—O_2 binding energy. In addition, as the assisted ion energy is increased from 0 to 200 eV, Si 2p peak shifted to higher binding energy due to the electric discharge given off by the insulating SiO_2 layer under 100% O_2 environment, which is usually observed in homogenous SiO_2 thin films. From the shift in the binding energy, the possible presence of neither Si column grown from the substrate nor Si island formed inside the SiO_2 matrix has been excluded.[21] The formation of homogeneous silicon oxide thin film resulted from ion bombardment during deposition process, which enhances diffusion and selectively deposits oxides on the region damaged by the ionized oxygen.

The O1s binding energy peak at various O_2-assisted ion energy level is shown in Figure 4(b). When assisted ion energy increased from 0 to 100 eV, O1s peak shifted 0.6 eV to higher binding energy similar to that of Si 2p peak. Consequently, observed shift in 2p and 1s peak of Si and O in the Si—O_2 bonding could be also correlated to the FTIR results.

Surface properties and optical properties

The surface morphologies of the silicon oxide thin films deposited on the PC substrate at room temperature under different O_2-assisted ion energies were observed using AFM as shown in Figure 5. Island growth mode was dominant when assisted ion energy

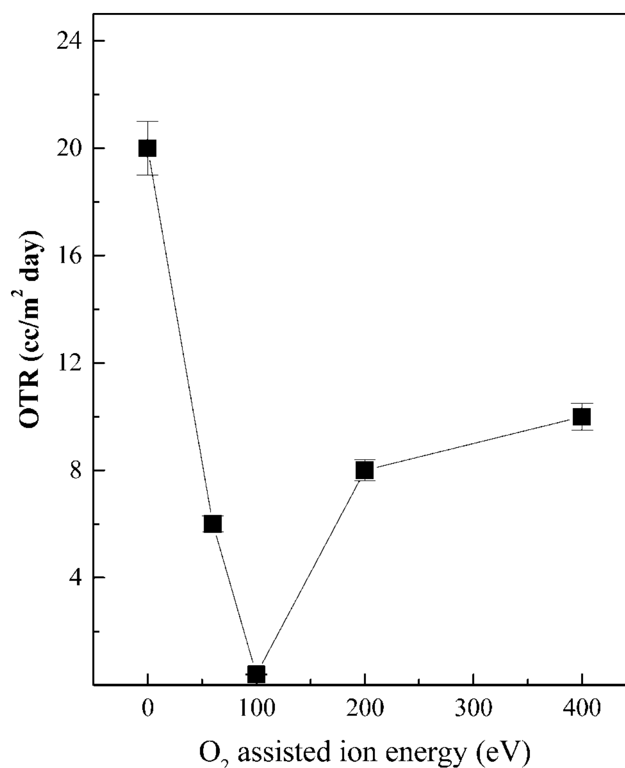
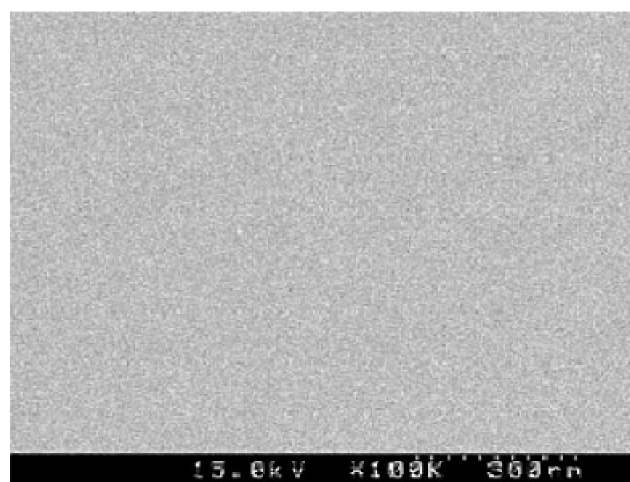
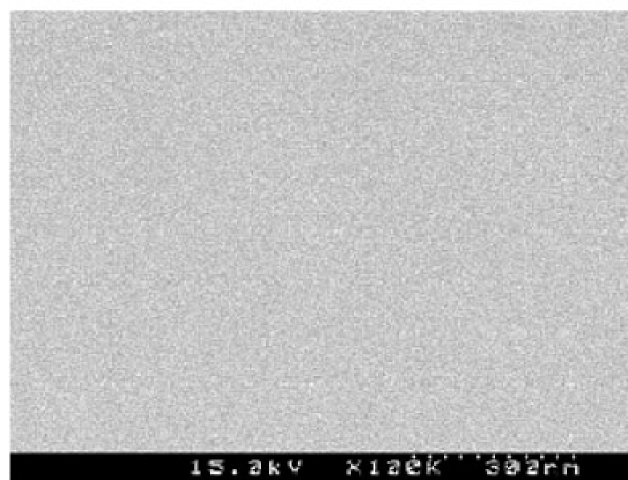


Figure 9 Oxygen transmission rate (OTR) of silicon oxide thin film on PC substrate deposited by O_2-assisted sputtering as a function of oxygen ion energy.



(a)



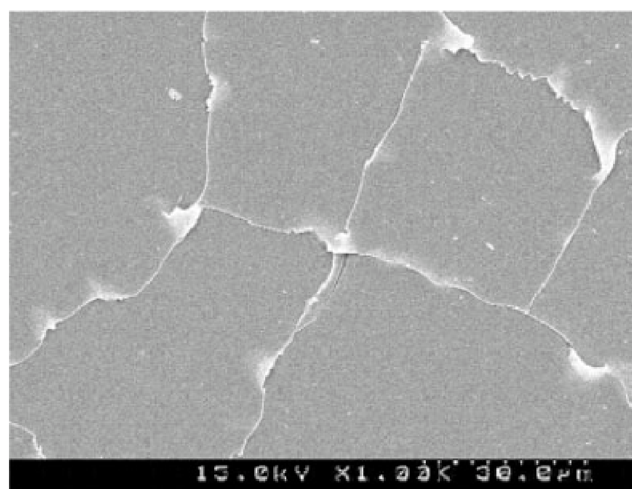
(b)

Figure 10 SEM photographs of silicon oxide thin film on PC substrate prepared by O_2-assisted sputtering with varying oxygen ion energy: (a) 100 eV, (b) 60 eV.

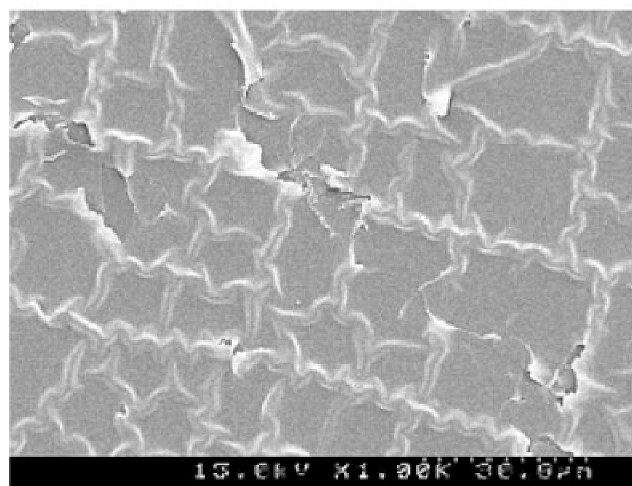
was between 0 and 60 eV, giving thin film with smooth and homogeneous surface morphology.

Combination of island and layer growth mode was observed at 200 eV. When assisted ion energy was increased to 400 eV, which is higher than critical ion energy, thin film with rough surface was obtained due to the surface damages caused by the resputtering effect. These results can be correlated to the increase in surface mobility of adatom at certain energy level. Rough and abrupt surface was obtained when no ion bombardment was applied at 0 eV and corrugated hill-shaped morphology was obtained even at 60 eV due to lack of energy supplied for surface diffusion of assisted O_2 ions. However, thin film with relatively smooth and homogeneous surface profile was obtained at 100 and 200 eV, indicating that the diffusion of oxygen atom has increased by ion bombardment. Therefore, the roughness of the thin film can be associated to the changes in the surface morphology. Figure 6 show the surface roughness of silicon oxide thin film on PC substrate deposited with varying assisted ion energy.

The surface roughness decreased from 1.7 to 0.4 nm as the ion energy is increased from 0 to 100 eV. Slight increase in surface roughness to 0.6 nm was observed at 200 eV but increased significantly to 1.5 nm when ion energy was further increased to 400 eV. Such a change in surface roughness affected by the assisted ion energy is expected to give similar trend on the OTRs. Refractive index has been measured for thin film obtained at different assisted ion energy as shown in Figure 7(a), since refractive index is directly related to the density and stoichiometry of the silicon oxide



(a)



(b)

Figure 11 SEM photographs of boiled silicon oxide thin film after 2 h at different deposition processing: (a) O_2-assisted and (b) nontreated PC.

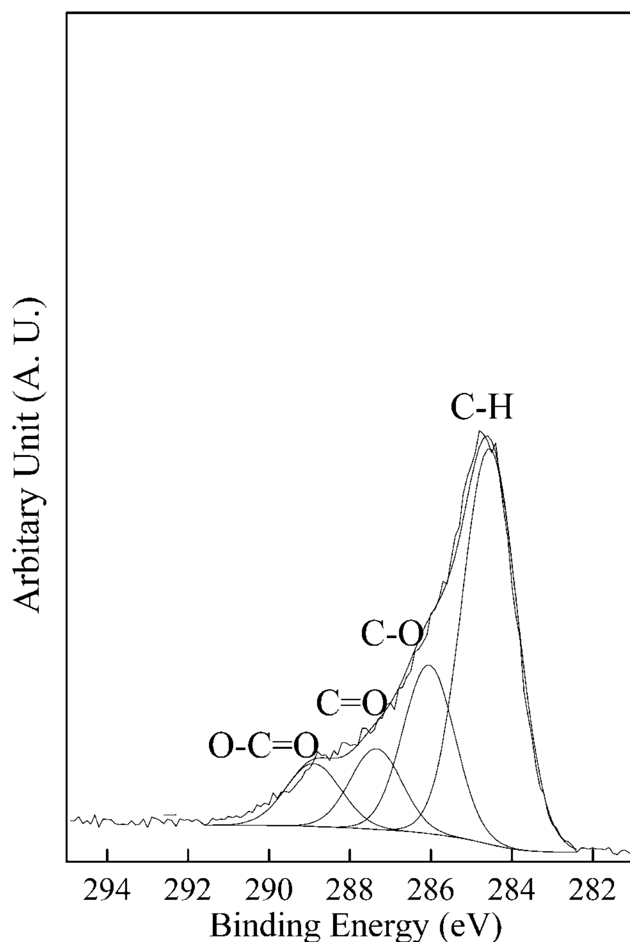


Figure 12 XPS C 1s core level spectra in case of O_2-assisted PC.

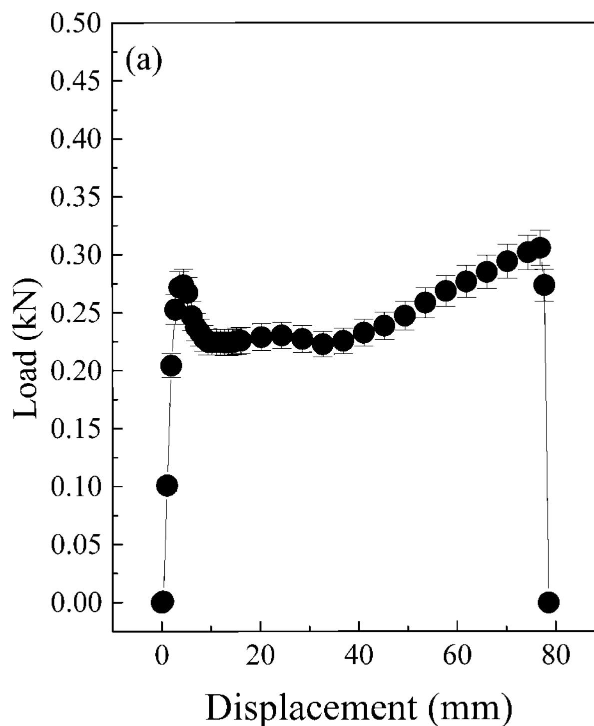
thin film. At 100 eV, refractive index was 1.45 similar to that of bulk SiO_2 but decreased to 1.35 when ion energy was further increased to 400 eV. Such results can be related to our previous surface morphology and stoichiometry studies, where the assisted ion energy of 100 eV was most suitable condition for producing dense and smooth silicon oxide thin films. The relative density calculated from the refractive index versus assisted ion energy is shown in Figure 7(b). Similar trend between refractive index calculated using Lorenz-Lorenz equation and relative density has been observed.

Optical transmittance of the thin film obtained at different assisted ion energy is shown in Figure 8, where close to 90% transmittance at 550 nm wavelength has been measured except for the thin film obtained at 400 eV. The optical transmittance decreased to 86% for the thin film obtained at 400 eV due to surface damages created by high-energy ions.

Barrier properties

Figure 9 shows OTRs of thin films synthesized under different assisted oxygen ion energies. The OTR decreased from 20 to 0.5 cc m^{-2} day^{-1} as the assisted ion energy is increased from 0 to 100 eV but increased to 10 cc m^{-2} day^{-1} when ion energy was further increased.

Surface properties that affect the protective layer characteristics have been observed using SEM as



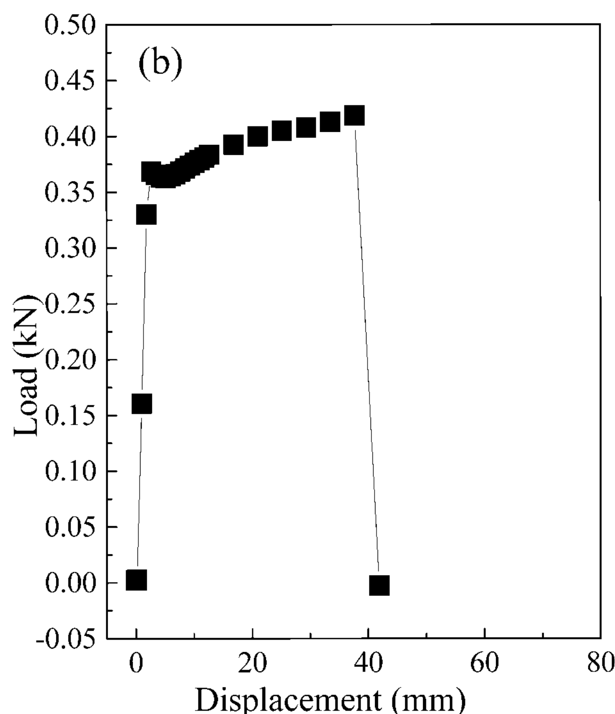


Figure 13 Load versus displacement of silicon oxide thin film deposited on (a) nontreated and (b) O_2-assisted PC.

shown in Figure 10 where no microsized defects have been observed for the thin film obtained at 60 and 100 eV. When OTRs of silicon oxide thin films were compared with that obtained by other techniques such as CVD and E-beam process, the OTR values were relatively lower showing that high quality thin film can be obtained by applying assisted ion beam during deposition. To indirectly confirm the formation of chemical functional groups on the surface of the substrate, which enhances adhesion between deposited silicon oxide thin film and the substrate by assisted ions during initial stage of the deposition process, boiling and tensile tests were conducted.

Figure 11 shows SEM micrographs of the silicon oxide thin film surfaces obtained by O_2-assisted process, immersed in boiling water for 2 h. Cracks appeared due to the difference in thermal expansion coefficients of the thin film and the substrate. However, no bloating effect was observed when compared with the thin film synthesized with surface treatment.

Improvement in adhesion can be anticipated due to the creation of new functional groups on the surface during initial deposition step using assisted ion implantation. Figure 12 shows C 1s core level after surface treatment using oxygen ion gun (100 eV), where hydrophilic functional groups (C=O, O—C=O) were present similar to that observed in deposition process with pretreatment step. To confirm the improvement in adhesion by these functional groups, the deposited thin film was subjected to the same boiling and tensile tests conducted on silicon oxide thin film deposited by ion-assisted sputtering.

Figure 13 is the tensile test results of the silicon oxide thin film obtained through O_2-assisted process. The strain at the crack was 40 mm, which is lower than that without surface treatment (a). This indicates that the crack occurred within the silicon oxide at lower strain when bonding is formed between thin film and substrate. From these results, improvement in adhesion at the interface between thin film and substrate by assisted ion process at the initial state of the deposition step has been confirmed. Consequently, silicon oxide thin film with similar oxygen transmission property was attained as that of pretreated process due to the improvement in the adhesion.

CONCLUSIONS

The interface properties between PC substrate and silicon oxide thin films have greatly influenced the OTR. To obtain the enhanced interface properties, we adopted the dual ion-beam sputtering process instead of introducing surface treatment. The silicon oxide thin films were prepared according to the oxygen ion energy, and the characterization of SiO_x thin films was conducted by chemical composition, surface morphology, and optical properties. The silicon oxide thin films with bulk stoichiometric ratio were obtained at critical deposition condition of 100–200 eV oxygen-assisted ion energy. The deposited SiO_x thin films at the critical condition presented lowest surface roughness with similar or higher optical transmittance than pure PC. Without pretreatment, we were able to accomplish the interface domination by the introduction of dual ion-beam sputtering, which was necessary for improving barrier properties of silicon oxide thin films.

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