Epitaxial growth of Ag films on native-oxide-covered Si substrates

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By employing radio-frequency magnetron sputtering, cube-on-cube domain epitaxy of silver films was accomplished on the Si(001) substrates that were initially covered with native silicon oxide. Energetic bombardment by sputtered Ag particles was found to play a critical role in the epitaxial growth, enabling desorption of native oxide at temperatures significantly lower than that reported in conventional thermal annealing in ultrahigh vacuum. Native oxide was found to desorb at temperatures as low as 200 °C as a result of kinetic interaction with the deposition flux. At deposition temperatures of 550 °C or above, native oxide was completely removed from the Si surface, and the grown films showed strong epitaxial relationship, Ag(001)[110]//Si(001)[110]. X-ray photoemission spectroscopy analysis confirmed that the desorbed silicon oxide migrated to the top surface of the Ag layer during sputter deposition.

PACS number(s): 68.55.−a, 68.35.Fx, 68.49.Uv

I. INTRODUCTION

Epitaxial growth of metal films on silicon substrates has been a subject of extensive studies over the past decades, since the material system potentially offers unique electronic, magnetic, or optical properties.[1] Ag on Si, a prototypical example of nonreactive metal and/or semiconductor system, can form a well-defined interface, offering a potential for ideal metal contact and Schottky barrier formation. While the bulk of the literature is available on the growth of Ag on Si surfaces cleaned in ultrahigh vacuum (UHV), relatively little has been reported on the growth in the presence of an adlayer. The presence of foreign atoms on a Si surface is expected to alter the growth dynamics and resulting film properties.[2–5] Shklyaev *et al.* and Barski *et al.* reported epitaxial growth of nanometer-sized Ge islands on Si surfaces covered with a thin silicon oxide layer.[3,4] A proposed mechanism was that a chemical reaction between Ge adatoms and SiO_x during deposition caused local desorption of the native oxide, inducing nucleation of epitaxial Ge nanoislands on the exposed Si surface areas. Presence of a native-silicon-oxide layer has also been utilized for the benefit of growing epitaxial silicides on Si. Post-deposition anneal treatment of Co layers, for example, has been reported to form epitaxial $CoSi_2$ on initially oxide-covered Si substrates.[5] The native-oxide layer was considered to serve as an initial diffusion barrier, retarding the metal-silicon reaction until the temperature reached the point of forming a desired silicide phase. Above a certain temperature, the metal atoms diffused through the thin oxide layer without chemical reaction, and then directly reacted with Si crystal forming an epitaxial silicide layer. An important difference between the Ag and Co cases is that Ag does not react with Si and therefore it does not easily form an alloy. In this work, we report epitaxial growth of Ag on initially native-oxide-covered Si substrates using RF magnetron sputtering. Energetic bombardment by sputtered Ag particles was found to desorb native oxide at deposition temperatures as low as 300 °C, significantly lower than that reported with conventional thermal annealing in UHV. Sputter deposition at 550 °C completely desorbed the native oxide, and a highly epitaxial Ag layer was obtained. The oxide removal observed in the significantly reduced temperature range is explained by the highly kinetic nature of sputter deposition (i.e., momentum transfer from sputtered Ag particles).

II. EXPERIMENTAL PROCEDURE

Ag films were grown on Si(001) substrates (*p*-type with resistivity of 20 Ω cm) using radio-frequency (RF) magnetron sputtering. The Si wafers were cleaned with solvents only (acetone, and methanol for 10 min each in an ultrasonic bath, and then rinsed in deionized water), not involving any acid solution. This cleaning process was intended to remove organic contaminants but to keep a native silicon-oxide formed on the Si surface. An alternative method was also employed in this work in order to prepare a Si surface covered with native oxide: the solvent-cleaned Si wafers were further processed by etching in a dilute HF solution, and then treated in a boiling solution of $HCl:H_2O_2:H_2O$ (3:1:1) for 5 min. This process is known to result in formation of 4–6 monolayers of SiO_x, called Shiraki oxide.[6,7] No difference was observed between the two substrate cleaning methods. The cleaned wafers were then loaded into a deposition chamber. The chamber base pressure was 10^{-6} Torr, and deposition was performed in Ar ambient (1 mTorr) at a substrate temperature ranging from room temperature to 600 °C. A 2-inch-diameter, 4*N*-purity silver target was used in conjunction with 4*N*-purity Ar gas for sputter deposition. Prior to ignition of plasma, the substrate temperature was raised to the desired point and stabilized in a 10-min time span. The plasma was then ignited and stabilized with a shutter closed. Film thickness was controlled by varying the deposition time. Deposition rate of Ag was approximately 0.2 nm/s at rf power density of 10 W/cm^2. The surface morphology and
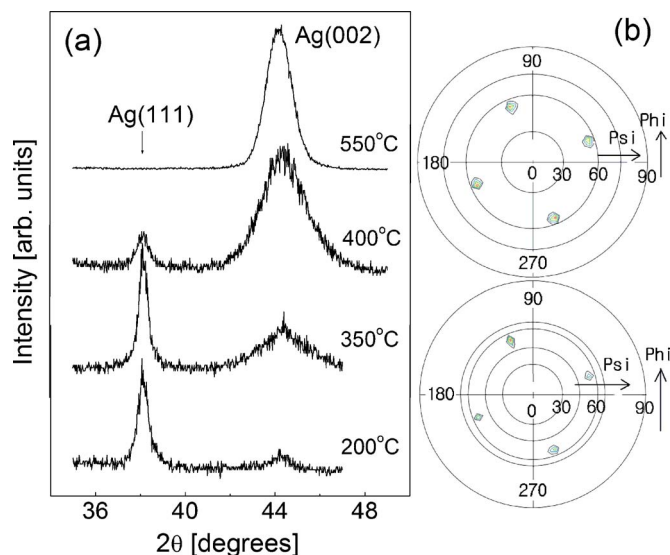
FIG. 1. (Color online) (a) XRD $\theta/2\theta$ scan profiles of Ag films that were sputter deposited for 40 s at different temperatures (200 °C, 350 °C, 400 °C, and 550 °C) on the Si(001) substrates initially covered with native oxide. (b) Pole figures from the 550 °C sample: the Ag(111) poles (top) and the Si(111) poles (bottom).

epitaxial properties of the deposited Ag films were investigated by scanning electron microscopy (SEM) and x-ray diffraction (XRD). Depth profiling of Si, O, and Ag contents was performed with x-ray photoemission spectroscopy (XPS) in conjunction with Ar ion beam sputtering.

III. RESULTS AND DISCUSSION

Figure 1(a) shows XRD $\theta/2\theta$ scan profiles of Ag films that were deposited for 40 s at various different temperatures (200 °C, 350 °C, 400 °C, and 550 °C) on Si(001) substrates covered with a native-oxide layer. The films deposited at room temperature are polycrystalline; the (111) reflection is dominant and some small peaks at higher 2θ are not shown in the figure. As the deposition temperature was raised above 350 °C, the dominance shifted to the (002) peak. At 550 °C the (111) peak disappeared and the (002) peak became the only one. Figure 1(b) shows the pole figures from the Ag film deposited at 550 °C and from a Si(001) substrate, respectively. The Ag(111) pole figure has a four-fold symmetry and perfectly matches the Si(111) poles, indicating an in-plane epitaxial relationship of Ag[110]//Si[110]. The observed tilt angle (Ψ =54.7 degrees) corresponds to the angle between the (111) and (001) planes in cubic crystals. Also the Ag (002) pole figure has a very strong central peak as expected (not shown). The lattice constants of Ag and Si are 4.09 and 5.43 Å, respectively, closely matching to a 3-to-4 ratio. It is clear that Ag(001) films were grown with cube-on-cube domain epitaxy on the Si(001) substrate, with a 4×4 mesh of Ag unit cells well matched to a 3×3 mesh of Si unit cells with a mismatch of 0.5%.[8] A remarkable point here is that epitaxial films were obtained despite that the Si substrate was initially covered with a native-silicon oxide.
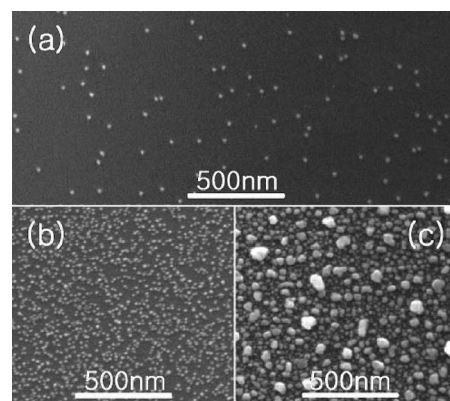

FIG. 2. SEM images of Ag films deposited at 550 °C for 40 s (a), 50 s (b), and 60 s (c).

Figures 2(a)–2(c) show SEM images of Ag films deposited at 550 °C for 40, 50, and 60 s, respectively. For deposition time of 10–35 s, the grown films were smooth and without any features that can be resolved by the SEM. This suggests that Ag might have grown in a two-dimensional-(2D) like growth mode in the early stage. Thickness of the Ag layer grown with 40 s deposition time [Fig. 2(a)] is estimated to be 8 nm, and the morphology shows scattered Ag nanoislands (of $\sim10^9$ cm^{-2} concentration) sitting on a 2D-like metal layer. As deposition time was increased to 50 s, the Ag island concentration increased to $\sim10^{11}$ cm^{-2} level. For 60 s or longer deposition time, the scattered islands formed a granular structure with a wide range of size distribution in both the lateral and vertical dimensions. From the plan view image of the 60 s sample, the lateral size of granular structure ranged from 10 to 100 nm.

Formation of epitaxial Ag on the native-oxide-covered Si surface is an intriguing result, considering the amorphous nature of silicon oxide. The oxide layer may block the template role of the crystalline Si surface, if the oxide still remains on the Si surface during Ag growth. The native oxide formed at room temperature is known to be about 2 nm thick with an oxygen content lower than that of thermally grown oxide (SiO$_2$).[9,10] Removal of native oxide from Si via gas phase desorption usually requires high temperature heating (at least 800 °C and usually performed at 1000 °C) in ultrahigh vacuum. Thermal stability of silicon oxide in a sputtering ambient, however, is not known. Considering the highly kinetic nature of in-coming sputtered particles, the thermal stability of native oxide might be significantly altered from that in the case of conventional thermal annealing in the UHV ambient. When sputter deposited with proper substrate heating, an oxide layer may easily desorb from the surface and diffuse through the Ag layer being deposited. The possibility of kinetically assisted thermal desorption of the native oxide was investigated by performing XPS depth profiling on chemical elements, Si, O, and Ag in the samples deposited at various temperatures (room temperature to 600 °C). (For depth profiling, thicker films were deposited with a deposition time of 90–300 s.) The depth profiles of these elements are expected to reveal information on possible dissociative and/or migrative behavior of native oxide during sputter deposition at various different temperatures.
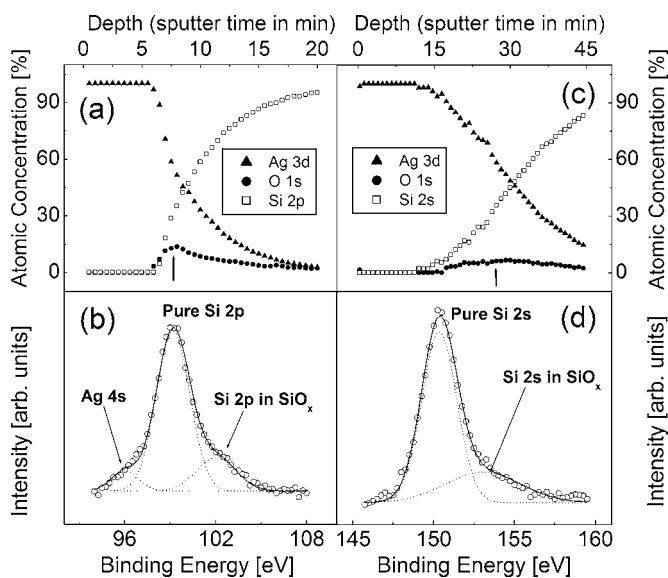
FIG. 3. XPS analysis results of the Ag films that were deposited at room temperature for 90 s (left-hand panel) and at 200 °C for 5 min (right-hand panel). The depth profiles of Ag, O, and Si concentrations are shown in the top panel. The energy spectra of Si and Ag measured at the film-substrate interface are shown in the bottom panel. Note the different energy ranges used for the spectra.
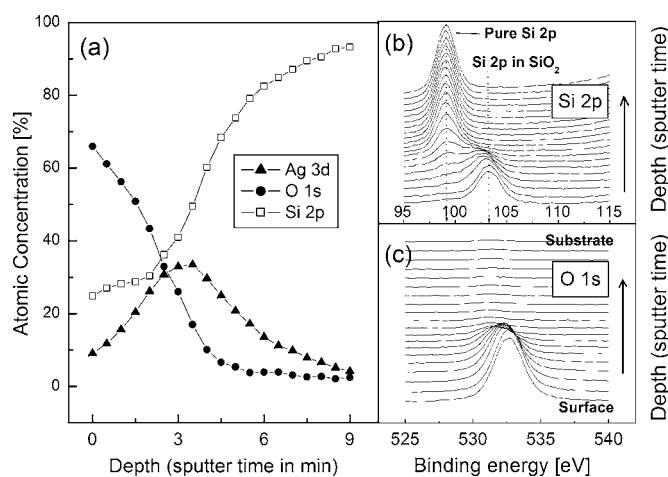

FIG. 4. XPS analysis result of a Ag film deposited at 550 °C for 90 s. (a) Depth profiles of Ag, O, and Si concentrations. (b) Depth profiles of Si $2p$ energy spectra. (c) Depth profiles of O $1s$ energy spectra.

Figure 3 shows the XPS analysis results of Ag films deposited at room temperature (a, b) and at 200 °C (c, d). The depth profiles of Ag, O, and Si contents (top panel), plotted as a function of sputtering time, are indicative of the layer structure, i.e., Ag layer, native oxide, and Si substrate in sequence from the top (top panel). The distribution of O content in the room-temperature-deposited sample clearly reveals a well-localized silicon-oxide layer (marked by an arrow) in the interfacial region between the Ag film and the Si substrate. Figure 3(b) shows an XPS spectrum (Si $2p$ level) of the room-temperature sample analyzed at the film-substrate interfacial region. A broad shoulder appears at ~ 102.0 eV on the high energy side of the main peak that corresponds to pure crystalline Si (at 99.2 eV). The XPS spectrum shows the Ag $4s$ signal at the low energy side of the pure Si peak. (For clarity, we subtracted the Shirley background and applied the Gaussian profile in order to fit the energy states.[11]) Si atoms in a native oxide have various different oxidation states (Si$^+$, Si^{2+}, Si^{3+}, etc.) with their corresponding Si $2p$ levels at $101-103$ eV.[12] The broad shoulder at ~ 102.0 eV reflects complex binding energies of Si atoms in a native oxide. In the 200 °C sample, the oxygen profile significantly broadened towards the Ag layer, whereas the Ag and Si profiles remained well confined in the film-substrate interfacial region [Fig. 3(c)]. This clearly indicates that the native oxide layer became less sharply localized, suggesting that a certain degree of oxide desorption and migration has already occurred at this temperature. The XPS spectrum (Si $2s$ level) analyzed at the interfacial region shows one major peak from pure crystalline Si (150.3 eV) and one broad shoulder that corresponds to oxidized Si (~ 153.0 eV) [Fig. 3(d)].

Figure 4 shows an XPS analysis result of the sample deposited at 550 °C for 90 s. The depth profiles are significantly different from those of the samples deposited at room temperature or 200 °C. The O profile shows complete depletion in the film-substrate interfacial region, indicating that native oxide was removed from the Si surface [Fig. 4(a)]. The O content sharply increased towards the film top surface. The Si profile has a significant extension to the top surface region, whereas the Ag content tapers off sharply. The depth profiles indicate presence of a SiO$_2$ layer formed on top of the Ag layer. The evolution of XPS spectra along the depth shows clear transitions of the energy states of Si and O. The XPS spectra of Si $2p$ shows a sharp transition from ~ 103.2 eV to 99.2 eV, which corresponds to a clear change from SiO$_2$ to pure crystalline Si in oxidation state [Fig. 4(b)]. The XPS spectra of O $1s$ at corresponding depths show absence of oxygen in the bottom part of Ag and strong presence in the top part as a O^{2+} state [Fig. 4(c)]. Overall the XPS result confirms that a native-oxide layer that initially existed on Si(001) surface completely desorbed and outdiffused to the top surface during sputter deposition at 550 °C. Formation of a SiO$_2$ layer on top of the Ag layer is evident from the clear binding states of Si and O that correspond to SiO$_2$. The presence of a stoichiometric oxide signal at the top surface suggests that the migrated native oxide SiO$_x$ became further oxidized into SiO$_2$ reacting with the oxygen molecules available from the ambient (with background vacuum level of 10^{-6} Torr).

According to the XPS and XRD analysis results, desorption of native oxide from local areas started to occur at around 200 °C. Around 550 °C the oxide desorbed from the entire Si surface. The oxide desorption is believed to have occurred with the arrival of deposition flux. Epitaxial nucleation occurred on the local oxide-free surfaces while the desorbed oxide outdiffused through the Ag layer being deposited. The binding strength of Ag atoms with their underlying layer would differ, depending on whether Ag atoms sit on a native oxide or they form an epitaxial layer nucleated on oxide-free Si surface. As such, adhesion of a Ag layer is expected to be significantly different between the two cases.
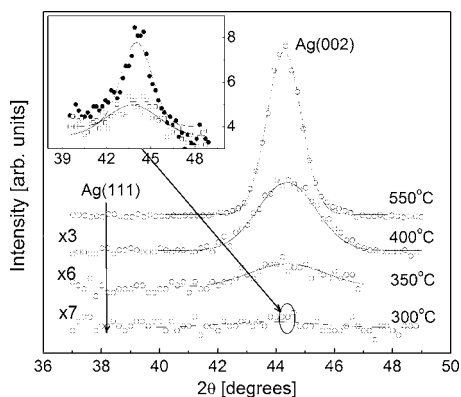
FIG. 5. XRD $\theta/2\theta$ scan profiles of the Ag films remaining on Si substrates after the film removal process. The Ag films were deposited for 40 s at 300 °C, 350 °C, 400 °C, or 550 °C. The inset shows a magnified view in the Ag(002) peak region of the 300 °C sample after the film removal process (empty square). The XRD before film removal is also shown for comparison (filled circle).

In order to reveal a possible adhesion contrast, a Ag film in the area of about 1 cm^2 was gently wiped off several times with a cotton-tipped applicator in acetone. The specimen was then cleaned in acetone in an ultrasonic bath for 5 min, followed by a rinse in methanol. Presence and the nature of any remaining layer on the Si substrate were then examined by XRD.

Figure 5 shows the XRD spectra of the samples that were grown at different temperatures (300 °C, 350 °C, 400 °C, and 550 °C) and were then treated with the physical removal process. Refer to Fig. 1 for the XRD spectra taken before the removal process. It is remarkable that the Ag(111) peak completely disappeared from the XRD spectra of all the samples grown at temperatures below 550 °C. In contrast, the Ag(002) peak still remains, although the intensity varies depending on the growth temperature. This suggests that the Ag layer deposited on top of the native-oxide-covered region was removed while the epitaxial Ag on the oxide-free Si region sustained. The intensity of the Ag(002) peak measured after the surface removal process monotonically increases as a function of deposition temperature. At around 400 °C, the peak intensity reaches 90% level of the intensity measured before removal. At 300 °C, the Ag(002) peak still appears after the removal, whereas at 250 °C the peak disappeared below the measurable range (not shown here). This result is consistent with the XPS and XRD analysis showing that the oxide desorption started in local spots at around 200 °C–300 °C and the desorbed area monotonically increased for higher deposition temperature.

Sputtered atoms impinging on a substrate are far more energetic than similar atoms emanating from an evaporation source. Without energetic atoms, substrate temperature would be the prime control variable that can influence the physical processes of film growth, i.e., physisorption and chemisorption, thermal desorption, nucleation, surface diffusion, etc. It is known that energetic atoms can influence all these processes at low temperature (i.e., without intentional heating of substrate).[13–15] The mechanisms of energetic film deposition have been studied with molecular dynamics simulations and kinetic Monte Carlo simulations.[14,15] Increasing the energy of the atom flux is known to have many effects that are analogous to an increase in substrate temperature. The native oxide layer on Si is expected to have a loose open structure, in view of the fact that even the thermal oxide, more stoichiometric than the native oxide, is known to have a certain degree of opening.[9,16] Energetic Ag atoms can penetrate through the oxide layer and reach the substrate surface. The kinetic energy of the impinging species is also channeled into enhancing the sticking coefficient and surface diffusion of adatoms, which is equivalent to increasing the substrate temperature in its effect on film growth. The process of adatom condensation and their incorporation into a film is known to be completed in a picoseconds to nanoseconds time frame.[15] An exchange process occurs simultaneously, in which a native oxide dissociates from the substrate surface and pops out as the incoming Ag atoms get incorporated into a surface layer. Once pushed out by energetic Ag atoms, the native oxide will diffuse to the top surface of a growing Ag film during deposition. The amount of Ag atoms that reach the Si substrate surface through the oxide layer and subsequently form epitaxial nuclei is expected to increase for higher substrate temperature, as indicated by the strong temperature dependence of the film property described above with XRD and XPS results. Out diffusion of native oxide through the Ag layer is also expected to be a strong function of temperature. The significant reduction of oxide-desorption temperature observed in this work, however, is mainly explained by the kinetic contribution from incoming sputtered particles.

In summary, this study reveals that native oxide on Si can be removed during sputter deposition at moderate temperatures, at least in the case of Ag deposition, and thereby epitaxial metal films can be grown without a separate rigorous process of oxide removal. This potentially offers great flexibility in designing processes for metallization on semiconductor substrates.

ACKNOWLEDGMENTS

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