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Characteristics of Ti-Capped Co Films Deposited by a Remote Plasma ALD Method Using Cyclopentadienylcobalt Dicarbonyl

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Co films were deposited by a remote plasma atomic layer deposition (RPALD) method using cyclopentadienylcobalt dicarbonyl $[CpCo(CO)_2]$ as the Co precursor with H_2 plasma. The impurity contents in the Co films were minimized under the optimized process conditions with H_2 plasma using a process pressure range between 0.1 and 2 Torr and a plasma power of 300 W. The ALD process window of the Co films showed a saturated temperature range between 125 and 175°C. The carbon and oxygen contents of as-deposited Co films were about 8 and 1 atom %, respectively. However, the carbon content in the Co films decreased from 8 to 4 atom % after in situ annealing at 400°C. For in situ annealed Co films deposited on Si substrates, a polycrystalline $CoSi_2$ phase was observed. The surface and interface morphologies of $CoSi_2/Si$ were rough compared to Ti-capped $CoSi_2/Si$ after ex situ annealing at 600°C. In addition, CoSi was completely transformed to $CoSi_2$ at 600°C. However, in the in situ annealed Co films with Ti-capped layer, the diffraction peak of $CoSi_2(200)$ began to appear at 700°C. The formation temperature of the Ti-capped $CoSi_2$ phase was retarded by about 100°C compared to the Co film without the Ti-capped layer. In addition, the surface and interface morphologies of the Ti-capped $CoSi_2$ layer were smooth.

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Metal silicides have been widely applied in advanced semiconductor devices such as ohmic contacts, gate electrodes, Schottky barriers, and interconnects.[1,2] Among the metal silicides, Co-silicide is considered as an excellent choice due to its good thermal and chemical stability, low resistivity, immunity to shrinkage of the line width, and close lattice mismatch with the Si substrate.[3,4] Because of these advantages, Co-silicide has been extensively investigated for application in ultralarge-scale integration (ULSI) devices. However, the use of Co-silicide can result in a rough interface formation and the incorporation of impurities such as oxygen.[5] A possible solution for these problems is to use a capping layer. In particular, the use of a Ti capping layer improves the interface roughness of Co-silicide. During annealing, the reactive Ti capping layer captures oxygen which is present in the interface and protects the silicide from oxygen contamination.[6] Many researchers have already reported that the uniform interface smoothness and thermal stability of the $CoSi_2$ layer were improved by using a Ti capping layer.[7,8]

To investigate the formation of Co-silicide, we applied an atomic layer deposition (ALD) method. Conventionally, a sputtering method has been the predominant deposition technique for $CoSi_2$ formation. However, the poor step coverage of the sputtering method becomes increasingly problematic in deep contact holes with high aspect ratio.[9] Moreover, the chemical vapor deposition (CVD) method offers advantages such as good conformal coverage and high growth rates but it generally introduces a large amount of impurities by gas phase reaction and a high deposition temperature.[10,11] Consequently, to overcome the shortcomings of conventional sputtering and CVD methods, we used an (ALD) method for this study.[12] Generally, using the ALD method, the precursor and reactant gas are introduced separately by maintaining a purge gas between the source and the reactants to prevent gas-phase reactions. Then, film growth by the ALD method is controlled by surface reactions through surface and self-limited mechanisms.[13] It is well known that the ALD method has many advantages such as ultrathin-film-growth capability, control of thickness, and elimination of particle generation due to gas-phase reactions.[14,15] Recently, reactive species such as ozone and plasma have been applied to improve the film quality in the ALD method. In particular, we applied the remote plasma ALD (RPALD) method to improve the film quality. This method was designed such that the substrate was placed out of the plasma region with the expectation that impurities and substrate damage would be reduced.[16] We previously reported that RPALD minimizes the problems caused by the use of a direct plasma.[17]

Employing the RPALD method, we deposited Co films using cyclopentadienylcobalt dicarbonyl $[CpCo(CO)_2]$ as the Co precursor. After Co deposition, Co films were characterized with transmission electron microscope (TEM), Auger electron spectroscopy (AES), and X-ray diffraction (XRD) to investigate their physical and chemical properties. We carried out the in situ annealing of Co films and the ex situ annealing of Ti-capped Co films at various temperatures. Then, we also investigated the variation of impurity content and interface morphology of the Co films as a function of the annealing temperature.

Experimental

Using the RPALD method with $CpCo(CO)_2$ as the Co precursor and H_2 as a plasma reactant gas, Co films were deposited on boron-doped p-type Si(100) substrates with a resistivity of 3–9 Ω cm. The Si substrates were cleaned by dipping in piranha solution ($H_2SO_4/H_2O_2 = 4:1$) for 10 min and then in a dilute hydrofluoric acid (HF) solution ($HF/H_2O = 1:50$) for 1 min to remove organics and native oxide, respectively, and then immediately loaded into the reaction chamber. A downstream-type RPALD reactor with a 13.56 MHz radio frequency (rf) power source was used in this study. One deposition cycle consisted of exposure to $CpCo(CO)_2$ cobalt precursor, a purge with argon, an exposure to H_2 plasma, and another argon purge. Argon purge gas was introduced to ensure the complete separation of the Co precursor and H_2 reactant gas. The H_2 gas flow rates were fixed at 20 sccm. The source injection time was fixed at 5 s for the $CpCo(CO)_2$ precursor. The processing times for the initial Ar purge, H_2 reactant plasma, and second Ar purge were 10, 20, and 10 s, respectively. The Co precursor was vaporized at 20°C for $CpCo(CO)_2$ and introduced into the reaction chamber using a bubbler with Ar as a carrier gas. In the previous study, we optimized the process condition. The growth rate of the Co films was about 1.1 Å per cycle in the ALD process window with a saturated temperature range between 125 and 175°C. Accordingly, Co films were deposited by the deposition temperature of 150°C with H_2 plasma using a process pressure range between 0.1 and 2 Torr at

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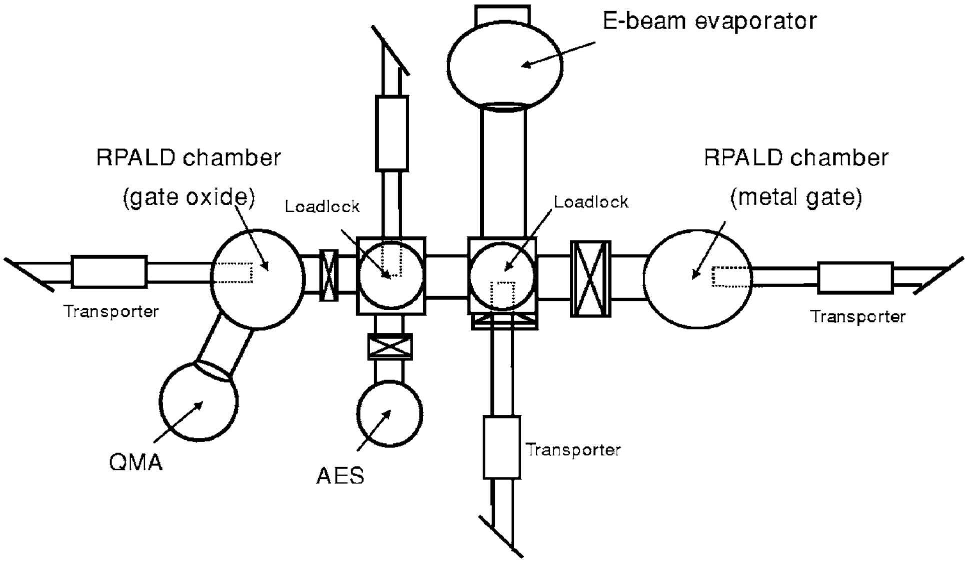

Figure 1. Schematic of cluster tool including RPALD system and E-beam evaporator.

the plasma power of 300 W. After Co deposition, the Co film was annealed in the reaction chamber without exposure to air. All samples were in situ annealed at 400°C. Then, a Ti capping layer with a thickness of 10 nm was deposited on the in situ annealed Co film by an e-beam evaporator without breaking the vacuum, as shown in Fig. 1. Subsequently, ex situ rapid thermal annealing (RTA) was carried out in N_2 ambient at temperatures between 500 and 800°C for 1 min. The chemical composition and impurity content were analyzed by AES. The phase identifications were carried out by XRD. The film thickness and microstructure of Co films were examined with cross-sectional transmission electron microscope (XTEM).

Results and Discussion

We investigated the impurity contents in the Co films on Si(100) substrates with and without in situ annealing. We also examined the interface morphology and the phase formation of Co-silicide with and without the Ti capping layer after in situ annealing. The variation of impurity contents in the Co films after in situ annealing was observed using AES. Kim et al. showed the AES depth profile of the Co film deposited by RPALD using $CpCo(CO)_2$ precursor at 150°C with H_2 plasma. The deposition rate of the ALD process for the Co film was ~1.1 Å per cycle with an ALD process window temperature between 125 and 175°C.[18] We also previously reported the process conditions of Co deposition in which the thickness of the Co film increased linearly with the number of cycles used in the ALD process window.[18] In that process, the impurity contents in the Co films were minimized using optimized conditions with H_2 plasma at a pressure range between 0.1 and 2 Torr and a plasma power of 300 W. The carbon and oxygen contents of the as-deposited Co films were about 8 and 1 atom %, respectively, and the oxygen content increased slightly at the interface of the Co film and Si substrate. The Cp ligand in $CpCo(CO)_2$ reacts in a reducing (H_2) atmosphere to form both stable and volatile hydrocarbons (C_xH_y) which are easily removed through the gas phase. The chemical reaction leading to the deposition of the Co film is generally represented by the equation $Co(C_5H_5)(CO)_2(g) + 1/2nH_2(g) \rightarrow Co(s) + 2CO(g) + C_5H_{5+n}(g)$.[19] Although the Co film deposited by RPALD using $CpCo(CO)_2$ precursor contained about 8 atom % carbon content, this is much lower than the approximately 50 atom % carbon content of Co films deposited by the metallorganic CVD (MOCVD) method using the same precursor and a similar H_2 pressure.[20] These results indicated that the reactive hydrogen radical in the H_2 plasma is more effective at breaking Co–Cp bonds than molecular hydrogen gas. Nevertheless, in order to lower the carbon content, the as-deposited Co film was treated with in situ annealing after Co deposition. In situ annealing was carried out in the deposition chamber without breaking the vacuum at a substrate temperature of 400°C. As a result, the carbon content in the Co film after in situ annealing decreased from about 8 to about 4 atom %, as shown in Fig. 2. However, the oxygen content in the Co film remained at about 1 atom %.

To investigate the phase identification of Co-silicide at various temperatures, in situ annealed 110 Å Co films without a Ti capping layer were taken out of the chamber, and ex situ annealing by RTA was performed at temperatures ranging between 500 and 800°C for 1 min in N_2 ambient. The phase identification was done with XRD, and the XRD patterns of Co-silicide formed on the Si substrate are shown in Fig. 3. XRD data showed that the (111) and (200) diffraction peaks of the $\beta - Co$ phase were observed with the in situ annealed Co film. After ex situ annealing at 500°C, the (210) and (211) peaks of the CoSi phase were observed by XRD analysis. It is usually reported that the silicide formation sequence of PVD-Co film, depending on the annealing temperature, is $Co_2Si \rightarrow CoSi \rightarrow CoSi_2$.[20] The phase transition fromCo_2Si to CoSi occurs at 350°C and the transition from CoSi to $CoSi_2$ occurs at 650°C. The

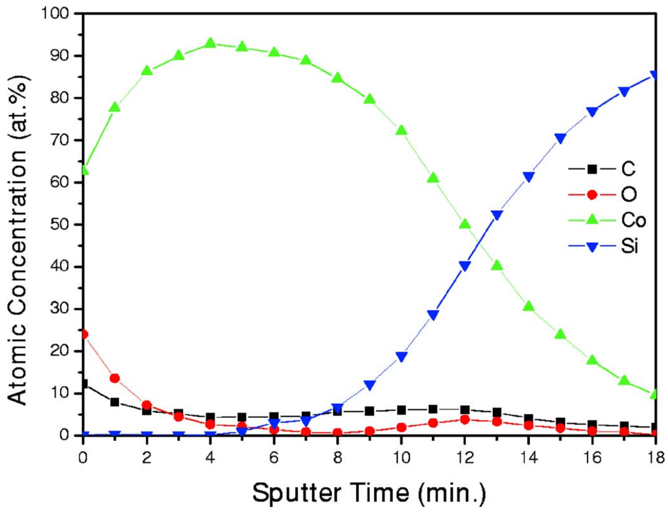

Figure 2. (Color online) AES depth profiles of in situ annealed Co films deposited by RPALD using $CpCo(CO)_2$ with H_2 plasma.

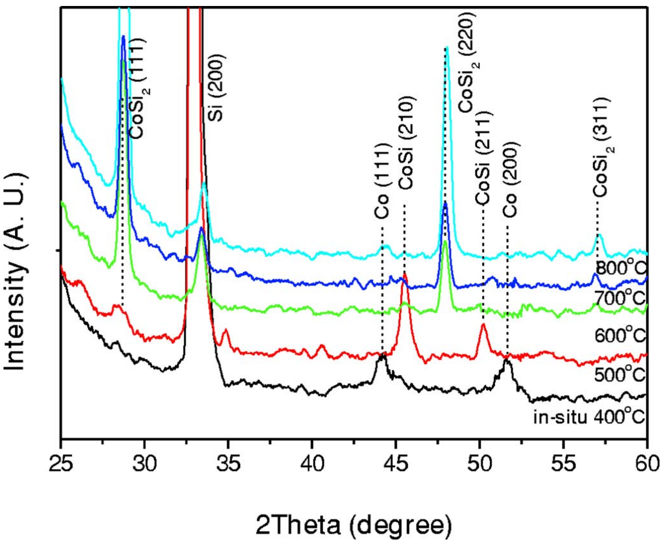

Figure 3. (Color online) XRD patterns of in situ annealed Co films deposited by RPALD using $CpCo(CO)_2$ with H_2 plasma after ex situ annealing at various temperatures for 1 min in N_2 ambient.

CoSi phase was formed from the Co film by ex situ annealing at 500°C. After ex situ annealing above 600°C, the (111), (220), and (311) diffraction peaks of $CoSi_2$ were observed without the (210) and (211) peaks of CoSi. Therefore, CoSi was completely transformed to $CoSi_2$ after ex situ annealing at 600°C. However, the phase transition temperature of $CoSi_2$ decreased from 650 to 600°C. This indicates that the formation temperature of $CoSi_2$ was slightly decreased due to the decreased impurity contents (carbon 4 atom % and oxygen 1 atom %) as a result of in situ annealing. We also observed a sharp further increase of the intensities of the $CoSi_2$ peaks up to an annealing temperature of 800°C.

To observe the interface and surface morphologies of Co silicides at various temperatures, we examined Co silicides with cross-sectional TEM. The thickness of the in situ annealed Co film was found to be about 110 Å, and this Co film showed a uniform surface and a smooth interface as shown in Fig. 4a. Figure 4b shows that the formation of the CoSi film appeared in the annealed Co film after ex situ annealing at 500°C as shown in the XRD data (Fig. 3). Also, the thickness of the CoSi film increased slightly. This indicated that Si atoms diffused into the Co film and formed CoSi. In particular, in the case of Co silicide formation, the volumetric change resulting from a Co film changing to CoSi increased about 1.81 times during silicide formation.[21] After ex situ annealing at 600°C (Fig. 4c), discontinuous $CoSi_2$ islands were formed, resulting in a rough surface and interface of the $CoSi_2$/Si substrate. In addition, cross-sectional TEM of the Co film after ex situ annealing at 700°C exhibited $CoSi_2$ recession and $CoSi_2$ island growth corresponding to the XRD data, as shown in Fig. 4d. The surface and interface morphologies of the Co film without the Ti capping layer after ex situ annealing were rough due to the agglomeration during the silicide formation reaction.[22] Later, we deposited a Ti capping layer to observe the change of the surface and interface morphologies during $CoSi_2$ formation.

From the above result, we applied a Ti capping layer to prevent the agglomeration of the Co film and to obtain a smooth surface and interface characteristics. The Ti capping layer was deposited on the in situ annealed Co film at 400°C by an e-beam evaporator and then Ti capped Co films were treated by ex situ annealing.[22] The interface microstructure and the phase identification of Co films with the Ti capping layer were observed by TEM and XRD analyses. Figure 5 shows the XRD patterns of Co films with the Ti capping layer after ex situ annealing in the temperature range between 600 and 800°C. The diffraction peak of $CoSi_2$(200), which is coherent with the Si substrate, began to appear after annealing at 700°C. However, the diffraction peaks of CoSi such as (210) and (211) and the diffraction peaks of $CoSi_2$ such as (111), (220), and (311) were not observed at all temperatures. Comparing the XRD data taken from the Co films with and without the Ti capping layer, polycrystalline $CoSi_2$ characterized by the diffraction peaks of (111), (220), and (311) was observed in case of the Co film without a Ti capping layer (Fig. 3). However, the diffraction peak of $CoSi_2$(200) appeared in

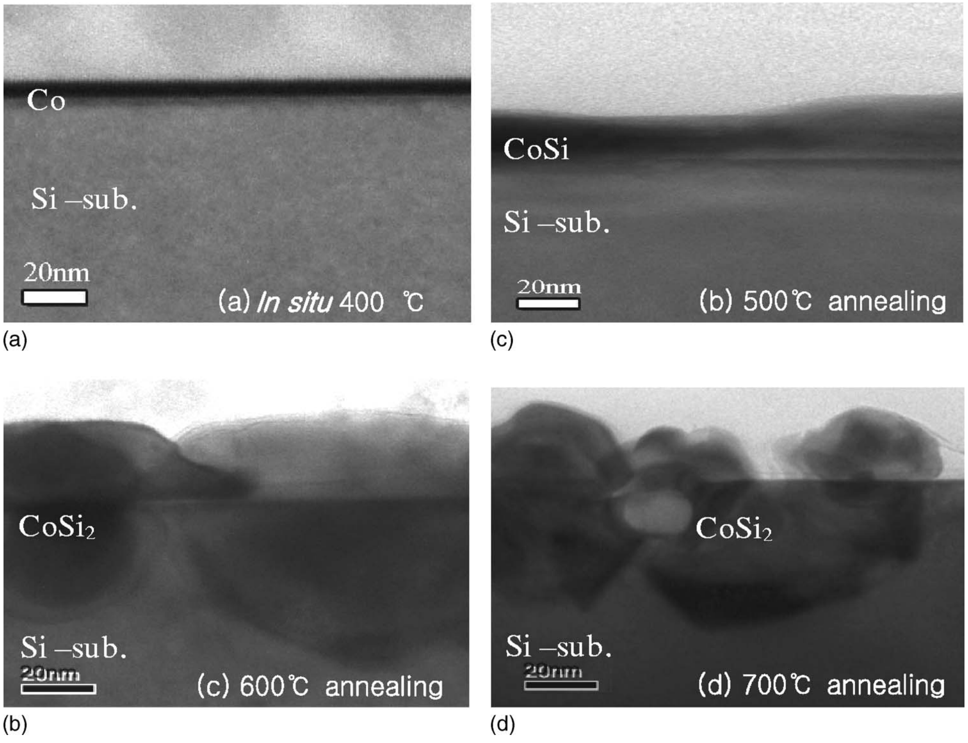

Figure 4. XTEM micrographs of Co films (a) in situ annealed at 400°C and ex situ annealed at (b) 500, (c) 600, and (d) 700°C deposited by RPALD with H_2 plasma.

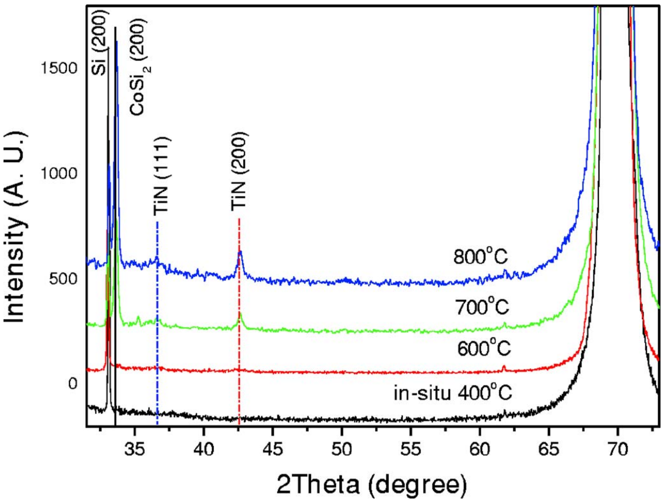

Figure 5. (Color online) XRD patterns of Ti-capped Co films deposited by RPALD using $CpCo(CO)_2$ with H_2 plasma after ex situ annealing at various temperatures for 1 min in N_2 ambient.

the case of the Co film with a Ti capping layer, as shown in Fig. 5. In particular, the formation temperature of the $CoSi_2$ phase was retarded about 100°C compared to the Co film without a Ti capping layer. In the case of Co with a Ti capping layer, it was reported that the phase transition temperature increased due to the penetration effect of Ti into the Co film during silicide reaction.[23] Furthermore, the (111) and (200) diffraction peaks of TiN were observed above 700°C RTA in N_2 ambient by XRD data, as shown in Fig. 5. The reason why the Ti layer changed into a TiN layer after ex situ annealing was that nitrogen atoms diffused into the Ti capping layer during high-temperature annealing, and the Ti atoms reacted with the nitrogen atoms.

As shown in Fig. 4, Co films without a Ti capping layer showed rough surface and interface morphologies. To investigate the effect of the Ti capping layer, a Ti layer was deposited on the Co film and annealed at 700°C for 1 min RTA in N_2 ambient. Figure 6 shows the AES depth profile of the Co film with a Ti capping layer and the cross-sectional TEM with two distinct layers on the Si substrate. The top layer is considered to be a TiN layer where the nitrogen came from the N_2 annealing ambient and then reacted with the Ti capping layer. The second layer is a Co-silicide layer where the atomic ratio of Co to Si was approximately 1:2, as shown in Fig. 6a. Also, the AES depth profile exhibits high oxygen impurity levels in the TiN layer and carbon impurities between the TiN and Co-silicide layers. In addition, the TEM of Co with a Ti capping layer film shows highly uniform surface and interface morphologies as shown in Fig. 6b. The interfaces of both TiN/$CoSi_2$ and $CoSi_2$/Si are very planar and smooth.

Conclusion

In conclusion, Co films were deposited by RPALD using cyclopentadienylcobalt dicarbonyl $[CpCo(CO)_2]$ as the Co precursor with H_2 plasma as a reactant at a process pressure range between 0.1 and 2 Torr and a plasma power of 300 W. The carbon and oxygen contents of as-deposited Co films were about 8 and 1 atom %, respectively. However, the carbon content in the Co film decreased from about 8 to about 4 atom % after in situ annealing at 400°C. In the case of the in situ annealed Co film without a Ti capping layer, polycrystalline $CoSi_2$ characterized by diffraction peaks of (111), (220), and (311) was observed after ex situ annealing at 600°C. However, the surface and interface morphologies of the $CoSi_2$/Si were very rough. In the case of the Co film with a Ti capping layer, the interfacial morphologies of both TiN/$CoSi_2$ and $CoSi_2$/Si were very planar and smooth after ex situ annealing at 700°C.

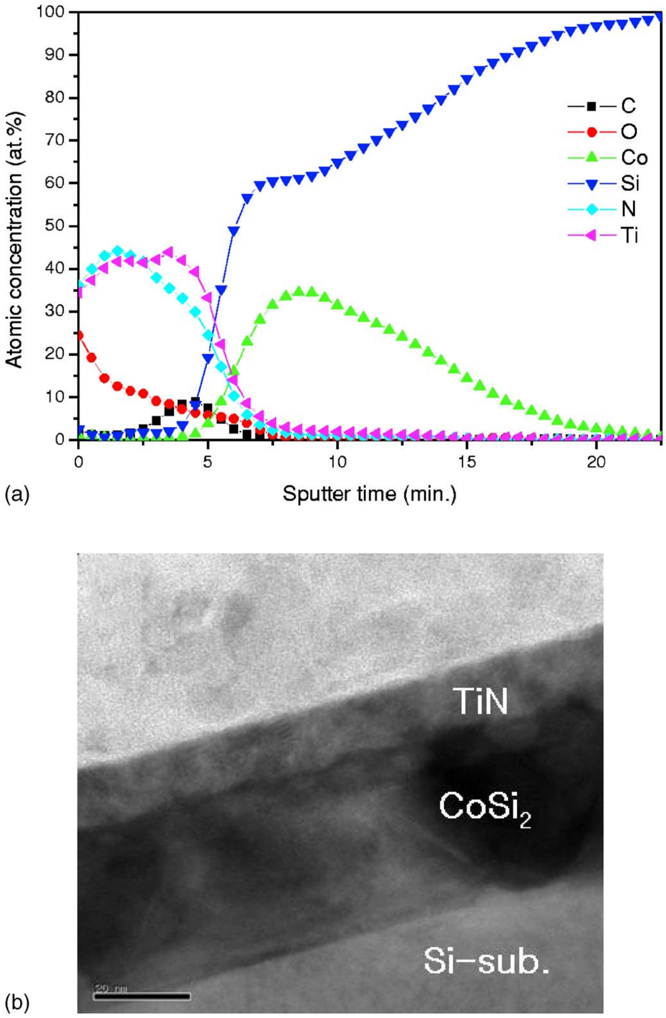

Figure 6. (Color online) (a) AES depth profile and (b) XTEM micrograph of a Ti-capped Co film deposited by the RPALD method after ex situ annealing at 700°C for 1 min in N_2 ambient.

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