

Highly Conformal Deposition of Pure Co Films by MOCVD Using $Co_2(CO)_8$ as a Precursor

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Highly conformal Co thin films were deposited on SiO₂ trenches with an aspect ratio of 13 by metallorganic chemical vapor deposition (MOCVD) using $\text{Co}_2(\text{CO})_8$ as a precursor in a low-temperature regime of 50–70°C where the growth rate was 3.5–7.0 nm/min. Lowering the pressure of the process reduces the number of collisions in the gas phase and, thus, widens the temperature regime in which the surface reaction controls the growth rate. A processing pressure of 26.7 Pa (0.2 Torr) allows for conformal deposition only at 50°C, whereas deposition at a reduced pressure of 4.0 Pa (0.03 Torr) widens the temperature regime (50–70°C) in which excellent conformality can be obtained. The conformal Co thin film, produced at 50°C and 4.0 Pa, showed a resistivity of 10–12 μ Ω cm and contained 1.0 atom % oxygen and less than 1.0 atom % carbon. After annealing this film at 600°C, its resistivity was reduced to 6 μ Ω cm, which is close to the bulk resistivity (5.7 μ Ω cm) of Co. Therefore, this low-temperature process, which allows for the excellent conformal deposition of pure Co films, can be utilized to produce silicided contacts for advanced devices which require a low contact resistance and good electrical performance. © 2006 The Electrochemical Society. [DOI: 10.1149/1.2189950] All rights reserved.

Manuscript submitted September 19, 2005; revised manuscript received February 13, 2006. Available electronically April 11, 2006.

Titanium has been widely used to form good ohmic contacts to heavily doped Si in metal oxide semiconductor (MOS) devices because of its ability to reduce the native oxide layer on the Si surface and the fact that the Schottky barrier height of Ti on n-Si is equal to approximately one half the silicon bandgap.¹ However, since the scaling down of these devices to dimensions below 100 nm, it has been found that the Ti layer has the drawback of increasing the contact resistance, especially in p-type (PMOS) devices, due to the rapid depletion of the boron in the p-type junction, which results from the high reactivity of Ti with boron (TiB₂, $\Delta G_{\rm f}$ = -319.6 kJ/mol).^{2,3} Compared with Ti, Co is less likely to form the corresponding boride (CoB, $\Delta G_{\rm f} = -92.5$ kJ/mol) and, thus, is less likely to cause the depletion of boron in the B-doped junction of PMOS devices. As a result, the use of Co in the P+ contacts of these devices provides for a much lower contact resistance than that of Ti.² Therefore, Co has rapidly replaced Ti in advanced devices.⁴⁻⁶ However, when it is used to deposit Co, the conventional physical vapor deposition (PVD) method exhibits a lack of conformal coverage and, thus, is not able to produce uniform, conformal thin films in sub-0.1-µm devices with complex shapes and structures. Therefore, most of the current research appears to focus on the use of chemical vapor deposition (CVD) as a unique conformal deposition method.

Kang et al. reported the conformal coating of CVD Co films over high-aspect-ratio contacts, however, the level of carbon impurity in the films was found to be quite high, although this was able to be reduced to about 3 atom % with the addition of H₂. The atomic layer deposition of Co films was also attempted using bis(N,N')diisopropylacetamidinato)cobalt(II) at temperatures between 260 and 350°C, and was found to result in the excellent conformal deposition of the Co films, which showed a resistivity of 46 $\mu\Omega$ cm for the 40-nm-thick Co films.⁸ However, the growth rate of the Co thin films of less than 1.0 Å/min which is obtained using this method needs to be increased before it can be used for device fabrication. The most commonly used precursors for MOCVD Co are cobalt carbonyls due to the large number of such compounds having sufficient volatility. In addition, the cobalt center in the compound is in the zero-valent state and, thus, no reductant such as H₂ needs to be added to deposit pure cobalt. As a result, pure cobalt films with low

carbon contamination and a low resistivity of 5–10 $\mu\Omega$ cm are able to be produced using $Co_2(CO)_8$ as a Co precursor. $^{9-12}However$, the facile thermal decomposition of $Co_2(CO)_8$ can produce reactive Co carbonyl species such as $Co_2(CO)_7$ and $Co_4(CO)_{11}, ^{13}$ which may be the main contributors to the growth of the Co films. These reactive intermediate products created in the gas phase tend to degrade the conformality of the Co films over high-aspect-ratio contact holes structures.

Therefore, we investigated the effects of various experimental variables, including the processing pressure, temperature, and addition of Ar carrier gas on gas-phase collisional activation of the reactants, which is known to strongly affect the conformality and growth rate of Co films. Based on the understanding of the gasphase collisional activation on the growth and conformality of the films, which was obtained from this investigation, the process conditions were optimized in order to obtain uniform, conformal thin films of Co. Finally, the quality of the conformal Co thin films was investigated.

Experimental

Cobalt was deposited on either SiO₂-coated or trench-patterned wafers by metallorganic chemical vapor deposition (MOCVD) using dicobalt octacarbonyl, $Co_2(CO)_8$, as a precursor. The trenchpatterned wafers, consisting of 0.2-µm-wide and 2.6-µm-deep SiO₂ trench structures on Si, were used to investigate the influence of pressure, temperature, and the addition of Ar carrier gas on the conformality of the Co films. The deposition was carried out at a temperature of 50-200°C and a pressure of 4.0-80.0 Pa (0.03–0.6 Torr). The typical flow rate of the Ar (99.9999% purity) carrier gas was 5 sccm and the pressure was varied by using a throttle valve in the pumping line. The Co precursor was introduced into the reaction chamber without Ar carrier gas to obtain a minimum process pressure of 4.0 Pa. The Co bubbler was maintained at 35°C and the delivery gas line was kept at 40°C to prevent any condensation from occurring inside the lines. The MOCVD system consisted of a coldwall reactor with a halogen lamp heating system and was equipped with a mechanical pump. In addition, laser reflectance was used to monitor the variation in the in situ reflectivity from the substrate surface, which reflects the growth of Co on the substrate.

The sheet resistance of the Co films was measured using a fourpoint probe and the thickness measured by means of a surface profilometer. A θ -2 θ X-ray diffractometer (XRD), equipped with a Cu

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Figure 1. Arrhenius plot for MOCVD Co films as functions of temperature and process pressure.

tube, operated at 50 kV and 200 mA, with a monochromatic wavelength (Cu K α) of 0.154 nm, was used to identify the phase and texture of the films. Auger electron spectroscopy (AES) was employed to detect the impurities such as carbon and oxygen in the Co films. Field-emission scanning electron spectroscopy (FESEM) and atomic force microscopy (AFM) were used to examine the step coverage and surface roughness of the films, respectively.

Results and Discussion

Figure 1 shows the Arrhenius plot for the deposition rate of the Co films as functions of the temperature and pressure of the process. In the temperature range of 50-90°C, the Co growth rate rapidly increases with increasing temperature and processing pressure, indicating that the reaction is limited by the pressure-related process as well as by the surface reaction. The deposition of Co at an extremely low pressure of 4.0 Pa, with no Ar carrier gas, can provide two distinct temperature regimes. Between 50 and 70°C (regime I), there is a moderate increase in the deposition rate of Co with increasing temperature, while at temperatures above 70°C (regime II), a sharp increase in the growth rate of Co with increasing temperature can be seen. The low-temperature regime, regime I, would be expected to be surface-reaction-limited. In this temperature regime, the $Co_2(CO)_8$ precursor can be adsorbed on the surface and then be thermally decomposed to deposit metallic cobalt.¹³ As the temperature increases above 70°C (regime II), the precursor thermally decomposes to produce intermediate products such as $Co_2(CO)_7$, $Co_4(CO)_{12}$ in the gas phase, and it is this process which is responsible for the rapid increase in the growth rate with increasing temperature observed in this regime.

The thermal decomposition process of $Co_2(CO)_8$ in the gas phase to produce zero-valent cobalt particles consists of the following reactions⁹

$$2Co_2(CO)_{8(g)} \rightarrow Co_4(CO)_{12(g)} + 4CO_{(g)}$$
 [1]

$$\operatorname{Co}_4(\operatorname{CO})_{12(g)} \to 4\operatorname{Co} + 12\operatorname{CO}_{(g)}$$
 [2]

However, the decomposition of $\text{Co}_2(\text{CO})_8$ to $\text{Co}_4(\text{CO})_{12}$ and further to metallic Co is expected to be a complex process which can be comprised of several mechanisms. The CO group can be removed from $\text{Co}_2(\text{CO})_8$ and generate an electron-deficient complex, $\text{Co}_2(\text{CO})_7$. This cobalt carbonyl species further reacts with $\text{Co}_2(\text{CO})_8$ to yield an intermediate, $\text{Co}_4(\text{CO})_{12}$. In addition, this intermediate can produce a cascade of electron-deficient fragments, which in turn may react to form cobalt complexes with high nucle-



Figure 2. Cross-sectional scanning electron microscopy (SEM) images of the trenches with an aspect ratio of about 13:1 in which Co films were deposited using $Co_2(CO)_8$ at 26.7 Pa, (a) at 50 and (b) 60°C, respectively.

arity (high Co/CO ratio).¹³ From this mechanistic point of view, the gas-phase decomposition process can produce a variety of reactive cobalt carbonyl species with higher sticking coefficient compared with $Co_2(CO)_8$ and thus, allow for the increased concentration of the adsorbed precursors on the surface. This results in a much higher growth rate of Co in temperature regime II. Also the dipole interaction between the electron-deficient cobalt fragments and the SiO₂ surface should be an important factor in determining the nature and extent of the Co–SiO₂ surface interaction. In the case of the 4.0 Pa process, there is a transition temperature of 70–80°C, below which the deposition of the Co thin films is limited by the surface reaction and above which it is limited by the gas-phase collisional activation of the reactants.

Ar carrier gas (5 sccm) was introduced into the reaction chamber and the pressure was increased to 4.0–80.0 Pa by varying the pumping speed. Increasing the pressure significantly increases the growth rate, in part due to the increased number of collisions in the gas phase between the precursor and Ar carrier gas, and in part due to the increased partial pressure of the reactants. These gas-phase collisions may result in the increased collisional activation of the reactants in the gas phase, thereby leading to the production of reactive cobalt carbonyl species, which are major contributors to the increased growth rate. Therefore, the transition temperature seems to disappear as the pressure is increased from 4.0 to 4.0–80.0 Pa.

Further increasing the temperature above 90° C tends to cause the Co growth rate to level off. Additionally, the growth rate is likely to decrease as the temperature is further increased above 130° C. This can be attributed to the homogeneous reaction of the Co precursors, which results in their loss.⁹

The bottom coverage of the Co films over high-aspect-ratio trenches was investigated in the temperature range of $50-90^{\circ}$ C, in which the growth rate is competitively controlled by the gas-phase collision effects and the surface reaction. Figure 2 shows a cross-sectional FESEM image of the trenches with an aspect ratio of about 13 in which cobalt films were deposited using Co₂(CO)₈ at a pressure of 26.7 Pa and a temperature of $50-70^{\circ}$ C. Co films with a thickness of approximately 50 nm were uniformly coated on the walls of the narrow trenches at a temperature of 50° C, revealing a bottom coverage of 85%, as shown in Fig. 2a. However, the bottom coverage drastically decreased to 14% (Fig. 2b) and 7% when the temperature was increased to 60 and 70°C, respectively.

This abrupt reduction in the conformal coverage of the Co films at temperatures above 60° C can be attributed to the gas-phase collisional activation of the reactants, possibly resulting from the collisions between the Co precursor and Ar carrier gas. Because these gas-phase collisions are strongly influenced by the temperature and



Figure 3. Cross-sectional SEM images of the Co films deposited at a reduced pressure of 4.0 Pa and temperatures of (a) 50, (b) 60, (c) 70, and (d) 80° C, respectively.

pressure of the process, the pressure was decreased from 26.7 to 4.0 Pa by introducing Co precursors into the reactor without Ar carrier gas in order to lower the production of these activated intermediates.

Figure 3 shows the cross-sectional FESEM images of the Co films deposited on the walls of the trenches at a reduced pressure of 4.0 Pa and temperatures ranging from 50 to 80°C. Excellent conformal deposition of the Co films was obtained up to 70°C, as shown in (a-c). However, further increasing the temperature to 80°C caused the bottom coverage to be decreased significantly to about 2-3%, possibly due to the reaction in the gas phase. This result is consistent with the existence of two growth temperature regions that are apparent at 4.0 Pa and 50-90°C, as shown in Fig. 1. In the lowtemperature regime (50–70 $^{\circ}$ C), where the surface reaction controls the rate, conformal deposition of the Co thin films was obtained. In the high-temperature regime (70–90 $^{\circ}$ C), where the gas collision effect controls the rate, the conformality was significantly degraded. It can be understood from this that the transition temperature below which the reaction is surface-reaction-limited needs to be raised in order to widen the process window for the conformal deposition of the Co thin films, and this transition temperature is strongly dependent on the process pressure and the nature of the carrier gas.

The film quality of the Co thin films deposited in the temperature and process regime, which is suitable for the production of highly conformal coatings, was examined. Figure 4 shows the variation in resistivity of Co films deposited on Si substrates as functions of temperature and pressure. The resistivity of the as-deposited Co



Figure 5. XRD patterns of about 100-nm-thick Co films deposited on SiO_2 -coated Si wafers at 4.0 Pa with various temperatures.

films is in the range of 10–15 $\mu\Omega$ cm. In addition, the Co thin films deposited at 26.7 Pa and 50–60 °C show slight higher resistivity than any of those deposited at 4.0 Pa; however, the difference is within experimental error.

According to the XRD analysis, the as-deposited Co films at 4.0 Pa have a microcrystalline structure (Fig. 5). Additionally, AES analysis reveals very low carbon content in Co film deposited at 4.0 Pa and 50°C, as shown Fig. 6. The low content of carbon (below AES detection limit) in the as-deposited Co film deposited at 4.0 Pa provides evidence for the complete decomposition of the adsorbed precursor on the surface at the low temperature of 50° C.

About 100-nm-thick Co films were deposited at 4.0 Pa and 50°C on SiO₂-coated Si wafers and then annealed in a vacuum at 100–700°C. Figure 7 shows the variation in the resistivity of the Co thin films as a function of the annealing temperature. The resistivity rapidly decreases from 14 to 8 $\mu\Omega$ cm, as the annealing temperature increases from room temperature to 300°C, possibly due to grain growth in the Co films. The resistivity continues to decrease as the temperature is further increased, reaching 6 $\mu\Omega$ cm, almost equal to the bulk resistivity (5.7 $\mu\Omega$ cm) of Co, after heating at



Figure 4. Variation in the resistivity of about 100-nm-thick Co films deposited on SiO_2 -coated Si wafers with temperature and pressure.



Figure 6. AES depth profile of MOCVD Co film deposited on SiO₂-coated Si wafers at 50°C and 4.0 Pa.

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Figure 7. Variation in the resistivity of about 100-nm-thick Co thin films deposited on SiO_2 -coated Si wafers as a function of the vacuum-annealing temperature.

600°C. Figure 8 shows the XRD patterns of the annealed Co films at various temperatures. The as-deposited Co films consist of microcrystalline α -Co (hexagonal close-packed) structure, and the intensities of the α -Co phase increase as the annealing temperature is increased up to 400°C, corresponding to grain growth in the temperature range of 100–400°C. In addition, annealing at 600°C transformed the α -Co structure into β -Co (face centered cubic) with a strong Co(111) texture, indicating that a large amount of grain growth occurred by surface minimization. From these results, it can



Figure 8. XRD patterns of about 100-nm-thick Co films deposited on SiO_2 -coated Si wafers and annealed in vacuum at various temperatures.

be concluded that the extremely low temperature $(50-70^{\circ}C)$ and pressure (4.0 Pa) regime provides for excellent conformality over high-aspect-ratio trenches and produces pure microcrystalline Co thin films which are free of carbon contamination.

Conclusion

We investigated the effects of various experimental variables, including the pressure and temperature, on the growth rate, conformality, and film quality of Co films. The observed dependence of the growth rate on the temperature and pressure shows the existence of a transition temperature below which the deposition process is limited by the surface reaction and above which it is limited by the gas-phase collisional activation. Lowering the pressure significantly increases the transition temperature and thus widens the temperature window for excellent conformality. The 26.7-Pa process shows the transition temperature of about 50°C and provides for excellent conformality only at 50°C. Lowering the pressure to 4.0 Pa increases the transition temperature up to 70°C and widens the temperature window, which allows for the conformal deposition of Co. The widening of the temperature window for conformal deposition of Co may be due to the effective suppression of the gas-phase reaction in the extremely low pressure region. The growth rate of the conformal Co films was 3.5-7.0 nm/min, depending on the temperature and pressure. In addition, the as-deposited Co films deposited at 4.0 Pa and 50°C have a resistivity of 10 $\mu\Omega$ cm and low carbon content in it, indicating that the low temperature allows for the complete decomposition of the Co precursor. Therefore, it can be concluded that this extremely low temperature process, which allows for the conformal deposition of high-quality Co films, can be employed to produce silicided contacts for the advanced devices, which require a low contact resistance and good electrical performance.

Acknowledgments

This work was supported in part by the ERC program of MOST/ KOSEF (R11-2005-048-00000-0) and in part through the Center for Nanostructured Materials Technology by the Korean Ministry of Science.

Kookmin University assisted in meeting the publication costs of this article.

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