Organometallic chemical vapor deposition of cobalt and formation of cobalt disilicide

M. E. Gross, K. Schnoes Kranz, D. Brasen, and H. Luftman

Citation: Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena **6**, 1548 (1988); doi: 10.1116/1.584212 View online: http://dx.doi.org/10.1116/1.584212 View Table of Contents: http://avs.scitation.org/toc/jvm/6/5 Published by the American Institute of Physics

Organometallic chemical vapor deposition of cobalt and formation of cobalt disilicide

M. E. Gross, K. Schnoes Kranz, D. Brasen, and H. Luftman AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 4 January 1988; accepted 19 May 1988)

The deposition of Co thin films by organometallic chemical vapor deposition is reported. Co is of interest in very large scale integration technology as a catalyst for electroless plating of other metals and as a precursor to formation of CoSi₂. High purity, conformal films of Co are deposited by pyrolysis of Co₂(CO)₈ at 200 °C in vacuum. These films exhibit electrical resistivities of 5–10 $\mu\Omega$ cm and excellent adhesion to Si and SiO₂. CoSi₂ is formed by heating the samples at 700 °C. The CoSi₂ films resulting from reaction of the Co films with the Si substrate contain larger grains than the starting film and exhibit electrical resistivities of ~13–37 $\mu\Omega$ cm. Selective formation of CoSi₂ on patterned test wafers shows similar attributes.

I. INTRODUCTION

Low-temperature processing of integrated circuits is a critical goal as very large scale integration (VLSI) adopts submicron design rules. Problems relating to substrate damage and materials compatibility during deposition and subsequent processing are increasingly being addressed by technologies based on the use of organometallic precursors. Chemical vapor deposition (CVD) offers the advantages of conformal coverage and minimal substrate damage over physical deposition processes such as evaporation and sputtering.1 Organometallic chemical vapor deposition (OMCVD) additionally often provides lower temperature routes to desired materials than corresponding inorganic precursors. The most generally useful class of compounds for OMCVD are metal carbonyls due to the large number of such compounds having sufficient volatility for efficient transport. In addition, the metal centers in these compounds are formally in the zero-valent state and therefore, in theory, no reductant need be added to deposit pure metal. These advantages have been borne out in the deposition of a wide variety of metals from their respective carbonyls (Cr, Mo, W, Fe, Ru, Ni).²⁻¹⁰ Surprisingly, Co does not appear on this list.

The primary interest in Co for silicon-based integrated circuit technology is as the disilicide CoSi₂. Transition metal silicides are of particular interest for Ohmic contacts, lowresistivity gates, Schottky barriers, and interconnect structures in silicon-based integrated circuits because of their metal-like conductivities and materials compatibility with silicon. CoSi2 represents one of the lowest resistivity silicides of the transition metals and is of interest for contact metallization.11 Selective formation of CoSi2 can be achieved by reaction of a Co film, deposited on a device wafer, with the substrate Si forming the disilicide in windows where the Co and Si are in contact. Unreacted Co can then be removed by a selective etch. In this paper we report a process for depositing Co from the organometallic precursor dicobalt octacarbonyl $Co_2(CO)_8$. The deposited Co reacts with the Si substrate at higher temperatures to form CoSi₂.

II. EXPERIMENTAL

Dicobalt octacarbonyl, $Co_2(CO)_8$ was purchased from Alfa Chemicals and used without further purification. The material is an air-sensitive, dark orange solid and all manipulations were carried out under an argon atmosphere. Si(100), Si(111), Si(100) with 1000 Å of thermal oxide



HARVARD Ex. 2125 p. 2 IPR2017-00664

 (SiO_2) and test pattern wafers were used as substrates. Immediately prior to a deposition run the substrate was cleaned in a Pirhana acid etch, rinsed in distilled water, then dried in a stream of N₂.

A schematic diagram of the apparatus for deposition of Co is shown in Fig. 1. The three-zone furnace was equipped with changeable end plates to accommodate 3- or 5-in, diameter fused quartz tubes for deposition on 2- or 4-in. diameter wafers, respectively. Typically, the deposition process was as follows. A single preweighed substrate was loaded onto a quartz boat and positioned vertically in the furnace at the front of the second zone. The furnace was evacuated to about 75 mTorr then backfilled with Ar twice before the final evacuation. The second and third zones of the furnace were set to the desired deposition temperature, while the first zone was left off and was subject only to radiative heating from the other zones. Argon carrier gas was passed over the Co₂(CO)₈ source at a rate of 1.5 sccm. At this rate and with the source at room temperature (25 °C), a deposition time of 4 min produced an average Co film thickness of 0.10-0.15 μm on a 2-in. substrate. Comparable thicknesses on 4-in. substrates in the larger furnace tube required deposition times of 30 min. A baffle, consisting of a lattice of gas rods placed at the front of the tube, improved the uniformity of film thickness across the wafer from +40% to +15%. CoSi₂ was formed by placing the CVD Co films in the threezone furnace at 700 °C for 1.5 h under 5 Torr argon.

On removal from the furnace, films were characterized by several techniques. Average Co film thicknesses were calculated on the basis of weight gain. Actual Co thicknesses were determined with a stylus profilometer (Dektak II) on steps etched with a solution of CH3CO2H/HNO3/H3PO4/H2SO4 in the ratio 5:3:1:1. Thicknesses of the CoSi₂ films were determined by Auger depth profiling and Rutherford backscattering spectroscopy (RBS). Sheet resistance was measured using a four-point probe. Co resistivities were calculated using the measured film thickness. CoSi2 resistivities were calculated using a film thickness correction of 3.3 $\mu m \cos i_2/\mu m \cos derived$ from the bulk densities. Composition of the films was studied by x-ray diffraction, Auger electron spectroscopy (AES), and RBS. Film morphology was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

III. RESULTS

A. Selection of source materials

Selection of source materials for CVD of thin films from organometallic precursors must take into consideration the following factors: (1) the precursor must have sufficiently

TABLE I. Deposition conditions and properties of cobalt films.

Deposition temperature (°C)	Reaction time (min)	Film thickness (µm)	Resistivity $(\mu \Omega \text{ cm})$
200	4	0.14	11
300	15	0.10	24
400	60	0.03	33

J. Vac. Sci. Technol. B, Vol. 6, No. 5, Sep/Oct 1988

high vapor pressure at a convenient temperature to achieve effective material transport; and (2) the temperature of decomposition should also be low but sufficiently separated from the sublimation temperature to prevent depletion of the source. Clearly, complete decomposition of the organometallic to the pure metal is the ultimate goal. To this end, a consideration of the organometallic decomposition chemistry is pertinent. The oxidation state of the metal in an organometallic molecule is a useful formalism to employ in evaluating possible precursors. Bis(acetylacetonate) cobalt (II), $Co(C_5H_7O_2)_2$, was used in two previous studies for the deposition of Co.^{12,13} The Co center in this molecule is in the +2 oxidation state. Thus, the metal must be reduced to form the desired film and it might be expected that the decomposition proceeds less cleanly. In fact, hydrogen was necessary to achieve clean decomposition in the previous studies. We chose $Co_2(CO)_8$ for our studies based on the knowledge that the Co centers are formally in the zero-valent state. No additional reducing agent should be necessary for decomposition of the carbonyl to pure metal, thus simplifying the deposition process.

Previous work on the deposition of Ru affords a comparison between carbonyl and acetylacetonate complexes of that metal.⁹ Although Ru films are produced from both precursors, tris(acetylacetonate) ruthenium (III), Ru(C₅H₇O₂)₃, requires a deposition temperature of 500 °C, whereas deposition from triruthenium dodecacarbonyl, Ru₃(CO)₁₂, is optimized at 250 °C. Contamination from the oxygen of the acetylacetonate ligands appears at deposition temperatures of 600 °C, at which point formation of ruthenium oxide, RuO₂, becomes kinetically favored.

B. Cobalt film deposition

Co films were deposited from $\text{Co}_2(\text{CO})_8$ at 200, 300, and 400 °C. Depletion of the source increased with temperature as seen in Table I. For a typical deposition at 200 °C on a 4-in. Si wafer, a 30 min run produced a film with 1600 Å average thickness. This deposition rate of 53 Å/min remained constant over a 2 h period and showed no variation with Si or SiO₂ substrate. Auger depth profile analysis of the 200 °C film, shown in Fig. 2, revealed only surface contamination of



FIG. 2. Auger depth profile of Co film deposited at 200 °C on Si(100).

HARVARD Ex. 2125 p. 3 IPR2017-00664

1550 Gross et al.: Organometallic CVD of cobalt

carbon, oxygen, and chlorine due to atmospheric exposure; C and O levels in the bulk of the film were below the detection limits of 1.0% and 1.5%, respectively. Although only surface contamination of carbon and chlorine was observed in the 300 °C film, the oxygen signal did not disappear until 1.5 min of ion milling. (The milling rate was precalibrated to 300 Å of SiO_2 per minute.) This higher oxygen content is responsible for the higher resistivity values obtained in these films. Severe depletion problems were experienced in the 400 °C deposition so that it was difficult to produce films of thickness comparable to the lower temperature runs. Auger analysis of the thin films showed contamination levels comparable to those seen in the 200 °C films, namely, surface contamination that disappeared after 30 s of ion milling. All the films were uniformly reflective and continuous, as seen in the scanning electron micrograph (SEM) in Fig. 3(a) for the 200 °C sample. Carrier gas flow rates and system pressure were optimized for depositions at 200 °C and all further work discussed will refer to depositions at that temperature.

C. Cobalt film microstructure and characteristics

The x-ray diffraction pattern for the 200 °C film, shown in Fig. 4(a), is representative of all the films and is attributable to Co with no sign of any oxide phases. The film does exhibit a preferred growth orientation that is not related to substrate orientation. Further evidence of the film microstructure is revealed in cross-sectional transmission electron micrographs (TEM), shown in Fig. 5(a). Small irregular grain size is evident. In addition, the sharp edges of the Co and Si signals in the RBS spectrum shown in Fig. 6 imply that little interdiffusion occurs at the 200 °C deposition temperature film thicknesses calculated on the basis of weight gain agree well with those derived from RBS measurements.

The typical 1600-Å thick Co film has an average sheet resistance of $0.524 \Omega/\Box$. This gives a calculated resistivity of 8.4 $\mu\Omega$ cm. Electrical resistivities for the Co films varied in the range 5–10 $\mu\Omega$ cm, calculated on the basis of weight gain and four-point probe sheet resistance measurements, compare well with literature values of 9.8 $\mu\Omega$ cm.¹⁴

D. Cobalt disilicide: Formation, microstructure, and characteristics

The Co films deposited on Si at 200 °C were heated at 700 °C for 1.5 h to form $CoSi_2$, as analyzed by x-ray diffraction [Fig. 4(b)]. Heating at 550 °C for 1.5 h produced a



FIG. 3. SEM of (a) Co film deposited at 200 $^{\circ}$ C on Si(100); (b) same film after heating to 700 $^{\circ}$ C in Ar, 1/2 h.

J. Vac. Sci. Technol. B, Vol. 6, No. 5, Sep/Oct 1988



FIG. 4. X-ray diffraction spectrum of (a) Co film deposited at 200 $^\circ C$ on Si(100) and (b) heated to 700 $^\circ C$ in Ar atmosphere, 1/2 h.

mixture of $CoSi_2$ and CoSi; at 625 °C, $CoSi_2$ alone was formed. AES and RBS analyses of the 700 °C film confirmed the presence of a 1:2 Co:Si ratio, as seen in Figs. 7 and 8. This can be seen in the RBS spectrum from the spreading and drop in height of the Co signal and the appearance of a shoulder in the Si signal that extends to the surface edge of Si.



FIG. 5. Cross-sectional TEM of (a) Co film deposited on Si(100); (b) same film after heating to 700 $^{\circ}$ C in Ar, 1/2 h. Bright-field image.



FIG. 6. RBS spectrum of Co film deposited at 200 °C on Si(111). The vertical arrows mark the surface positions of the corresponding elements.

SEM and cross-sectional TEM photomicrographs, Figs. 3(b) and 5(b), respectively, show significantly more texture in these films than in the starting Co film. A calculation of the expected difference in film thickness based on the decrease in density between Co ($\rho = 8.9 \text{ g cm}^{-3}$) and CoSi₂ ($\rho = 5.3 \text{ g cm}^{-3}$) indicates that the CoSi₂ film should be 3.3 times as thick as the Co film. The film thickness derived from the RBS data agrees with the calculation. However, we observe thickness increases up to four times that of the Co film, as measured by cross-sectional TEM. The slightly larger increases reflect voids and random grain orientation in the silicide films.

Two features that stand out from the cross-sectional view in Fig. 4(b) are the large, columnar grains (\sim 5200 Å) and the rough interface. The nonuniform penetration of a thin film of native oxide at the Co/Si interface may inhibit the silicide-forming reaction, leading to a rough interface. It has been shown that formation of CoSi at 400 °C prior to forma-



FIG. 7. Auger depth profile of $CoSi_2$ formed by Co deposition at 200 °C and heating to 700 °C in Ar, 1/2 h.

J. Vac. Sci. Technol. B, Vol. 6, No. 5, Sep/Oct 1988



FIG. 8. RBS spectrum of CoSi_ film formed by Co deposition at 200 °C and heating to 700 °C in Ar, 1/2 h.

tion of CoSi_2 at 650 °C generates a smooth interface owing to a change in the dominant diffusing species in the two reactions.¹⁵ In our experimental arrangement, however, a higher temperature (> 500 °C) was required to achieve reaction, apparently owing to the inhibitory effect of the native oxide. The electrical resistivity of the CoSi_2 films formed at 700 °C was 13–37 $\mu\Omega$ cm, as compared with previously reported values of 18–20 $\mu\Omega$ cm.¹¹

IV. DISCUSSION AND CONCLUSIONS

Evidence of the conformal coverage of our OMCVD Co films can be seen in the high-resolution SEM of Si windows in SiO₂ (Fig. 9). The films, as formed, are slightly thicker at the top of the windows than on the sidewalls. Co was also deposited on Si in grooves etched in SiO₂ [Fig. 10(a)] and heated at 700 °C for 1.5 h to form $CoSi_2$ [Fig. 10(b)]. The grain structure after heating shows an increase in size and roughness similar to what we observed in the planar films discussed above. The break in the film on top of the SiO₂, seen in Fig. 10(b), was common and indicates a strain in the Co film caused by the silicide-forming reaction approaching from both sidewalls. We made no attempt to limit the reaction time to prevent silicidation of the Co on the SiO₂ steps.



FIG. 9. SEM of Co film deposited at 200 °C on Si windows in SiO2.

HARVARD Ex. 2125 p. 5 IPR2017-00664





(b)

FIG. 10. Cross-sectional TEM of (a) Co film deposited on Si grooves etched in SiO₂; (b) same film after heating at 700 $^{\circ}$ C in Ar, 1.5 h.

We have demonstrated a process for depositing high-quality Co films from $Co_2(CO)_8$ at the relatively low temperature of 200 °C. A higher (700 °C) temperature treatment leads to formation of $CoSi_2$ in what might be used as a selfalignment technology. The resulting $CoSi_2/Si$ interface is rough owing in part to the effects of the thin native oxide on the silicide reaction. *In situ* cleaning of the substrate in the deposition chamber should lead to a more uniform reaction front that, along with an initial lower temperature heating cycle to form CoSi, would allow for shallower junction depths. Co itself may find application in VLSI technology as a catalyst for electroless plating of other metals to fill in vias and connect multilevel metallization schemes. Recent interest in materials for contacts to III–V semiconductors has led us to investigate the formation of cobalt phosphides and cobalt arsenides from the triethylphosphine and triethylarsine derivatives of $Co_2(CO)_8$, namely $Co_2(CO)_6(XEt_3)_2$, X = P, As.¹⁶ Our work on the deposition of Co from $Co_2(CO)_8$ serves as a starting point and control from which to explore formation of a variety of binary materials using derivatives of the parent carbonyl.

ACKNOWLEDGMENTS

The authors thank T. T. Sheng and R. V. Knoell for the cross-sectional TEM's and R. D. Yadvish for wafer cleaning and preparation.

- ¹M. L. Green and R. L. Levy, J. Met. 37, 63 (1985).
- ²B. B. Owen and R. T. Weber, Met. Technol. **15** (1), Tech. Publ. No. 2306 (1948).
- ³J. J. Lander and L. H. Germer, Met. Technol. 14 (6), Tech. Publ. No. 2259 (1947).
- ⁴L. F. Kaplan and F. M. d'Heurle, J. Electrochem. Soc. 117, 693 (1970).
 ⁵A. I. DeRosa, D. B. Dove, and R. E. Lochman, J. Vac. Sci. Technol. 11,
- 455 (1974).
- ⁶M. Miyake, Y. Hirooka, T. Imoto, and T. Sano, Thin Solid Films **72**, 247 (1980).
- ⁷G. J. Vogt, J. Vac. Sci. Technol. 20, 1336 (1982).
- ⁸R. Kaplan and N. Bottka, Appl. Phys. Lett. 41, 972 (1982).
- ⁹M. L. Green, M. E. Gross, L. E. Papa, K. J. Schnoes, and D. Brasen, J. Electrochem. Soc. **132**, 2677 (1985).
- ¹⁰V. G. Syrkin and Yu. G. Kiryanov, J. Appl. Chem. USSR 43, 1076 (1970).
- ¹¹S. P. Murarka, Silicides for VLSI Applications (Academic, New York, 1983).
- ¹²R. G. Charles and P. G. Haverlack, J. Inorg. Nucl. Chem. **31**, 995 (1969).
 ¹³E. J. Jablonowski, Cobalt **14**, 28 (1962).
- ¹⁴CRC Handbook of Chemistry and Physics, 55th ed., edited by R. C. Weast (Chemical Rubber, Cleveland, Ohio, 1974).
- ¹⁵S. P. Murarka, J. Vac. Sci. Technol. 17, 775 (1980).
- ¹⁶M. E. Gross and J. Lewis, J. Vac. Sci. Technol. B 6, 1553 (1988).