

## Low temperature chemical vapor deposition of Co thin films from $\text{Co}_2(\text{CO})_8$

D.-X. Ye<sup>a,\*</sup>, S. Pimanpang<sup>a</sup>, C. Jezewski<sup>b</sup>, F. Tang<sup>a</sup>, J.J. Senkevich<sup>a</sup>,  
G.-C. Wang<sup>a</sup>, T.-M. Lu<sup>a</sup>

<sup>a</sup>Center for Integrated Electronics and Department of Physics, Applied Physics and Astronomy,  
Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

<sup>b</sup>Department of Physics, University at Albany, Albany, NY 12222, USA

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### Abstract

Cobalt thin films were deposited on the Si(100) substrates with temperatures ranging from 60 °C to 250 °C using chemical vapor deposition with a metallorganic  $\text{Co}_2(\text{CO})_8$  precursor. After Ar sputtering of the surface of the films, X-ray photoelectron spectroscopy (XPS) showed negligible O peak for all samples investigated. Analysis of high-resolution XPS Co and C peaks showed that a Co–C bond exists at high deposition temperatures of 140 and 160 °C. But pure Co peaks with no Co carbide bonding were observed for films deposition at 70 and 80 °C. Two growth rate maxima were observed at substrate temperatures of 120 and 220 °C using the Rutherford backscattering spectrometry. The two maximum growth rates are due to the transition from surface reaction controlled growth (60 to 140 °C) to mass-transport controlled growth (150 to 220 °C). The decrease of growth rate after the maximum growth rate was believed to come from a change in the decomposition pathways and the sticking coefficient.

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### 1. Introduction

There has been continual interest in cobalt thin films. Cobalt has been used as catalysts to grow aligned carbon nanotubes via chemical vapor deposition (CVD) [1–4]. It is also used as a catalyst in the Fisher-Tropsch synthesis, which forms alkanes from  $\text{H}_2$  and CO and higher order oxygenates [5]. Cobalt thin films are also of interest due to their high magnetic permittivity and have been recently investigated on nanostructured surfaces [6–8]. Furthermore, there are many reports of using cobalt thin films to form cobalt disilicide ( $\text{CoSi}_2$ ) for Ohmic contacts owing to its low resistivity in front-end-of-the-line processing of semiconductor devices.  $\text{CoSi}_2$  thin films were also recently studied

as Cu/low k barriers for ultralarge scale integrated devices [9–13].

High-purity cobalt thin films can be obtained by metallorganic chemical vapor deposition. Co thin films via CVD were shown to have a larger grain size than sputtered films and thus have a lower resistivity [14]. Furthermore, CVD can yield conformal cobalt thin films and cobalt alloy films with high purity. Commercially available CVD precursors for cobalt include cobalt carbonyl complexes [10–12,14–16], cobalt acetylacetonates [17] and cobalt acetate [18]. Recently, novel cobalt(I) hydride precursors were synthesized by Choi et al. and used to deposit high quality cobalt thin films at 300 °C [19]. Dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$ , has been extensively used in cobalt CVD and is attractive, since Co is in its elemental oxidation state and therefore no reducing agent is necessary for the deposition. In addition,  $\text{Co}_2(\text{CO})_8$  possesses high volatility at room temperature and thus can be sublimed in the absence of a carrier gas [16].

\* Corresponding author. Tel.: +1 518 276 8369; fax: +1 518 276 8761.

E-mail address: [yed@rpi.edu](mailto:yed@rpi.edu) (D.-X. Ye).

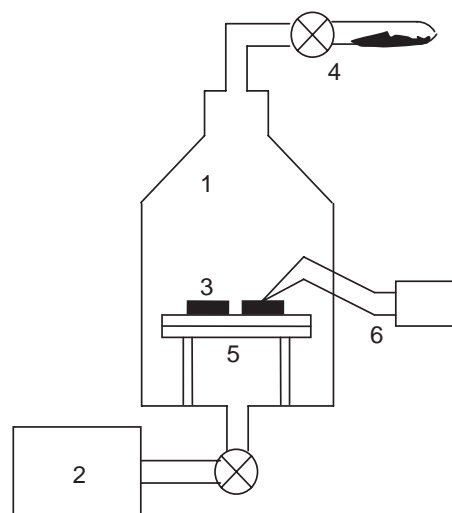
Finally, unlike other precursors, the deposition temperature of  $\text{Co}_2(\text{CO})_8$  can be low, ranging from 50 °C to 300 °C [10,14,15,20].

However, inconsistent deposition rates of cobalt thin films from  $\text{Co}_2(\text{CO})_8$  have been reported in the literature. There was one maximum deposition rate observed in the temperature range of 60 °C to 300 °C but the position of the maximum growth rate varied in the literature. H. Rhee et al. reported depositing cobalt thin films from  $\text{Co}_2(\text{CO})_8$  at temperatures between 150 °C and 300 °C. They observed that the deposition rate increases to a maximum of around 200 °C and decreases at a higher substrate temperature [10]. No deposition rate below 150 °C was reported by the same group. Y. Ko et al. observed a maximum deposition rate at ~140 °C [14]. However, D.W. Greve et al. reported that the maximum deposition rate is obtained at 175 °C from  $\text{Co}_2(\text{CO})_8$  under low deposition pressure conditions [15].

In this paper, we investigated the deposition rates of Co thin films as a function of deposition temperature ranging from 60 °C to 250 °C. Two maximum deposition rates were observed at 120 and 220 °C as measured by Rutherford backscattering spectrometry (RBS). We used X-ray photoelectron spectroscopy (XPS) to study the chemical quality of the deposited films. We report that high quality cobalt thin films, although with a lower growth rate, can be obtained at low deposition temperatures of 70–80 °C when compared with those deposited with a maximum rate at higher temperatures of 140–160 °C. We propose that the poorer quality films deposited at temperatures higher than 140 °C is due to the formation of cobalt carbide from the dissociation of CO on cobalt.

## 2. Experimental details

The vertical cold-wall CVD reactor designed for Co thin film deposition is schematically shown in Fig. 1. A resistance heater attached to the back of a substrate susceptor was used for substrate heating. The substrate temperature was monitored by a type K thermocouple and controlled by a temperature controller (CN76000, Omega Engineering, Inc., USA). The substrate temperatures are accurate to  $\pm 2$  °C. The inner wall of the CVD reactor was cleaned with acetone and dried prior to each deposition. Two pieces of Si(100) substrates with a native oxide were used without surface treatment for each deposition. After the substrates were mounted on the susceptor and the chamber was evacuated to  $\sim 10$  mTorr by a mechanical pump, the CVD chamber was flashed with 100 sccm Ar gas for 10 min. The heating-tape wrapped chamber wall and substrates were heated up to 120 °C with continuous Ar flow for 1 h to out-gas the system. The wall of the chamber was then cooled down to ambient temperature. After the substrate temperature was stabilized, the cobalt precursors were then introduced into the deposition



1. Chamber 2. Mechanical pump 3. Substrate  
4. Precursor reservoir 5. Susceptor and heater  
6. Thermocouple and controller

Fig. 1. A schematic drawing of the vertical cold-wall CVD reactor.

chamber without a carrier gas. The deposition time was 5 min for all experiments. The source was kept at room temperature ( $\sim 23$  °C) without external heating during the experiment. Dicobalt octacarbonyl,  $\text{Co}_2(\text{CO})_8$ , was purchased from Alfa-Aesar and used without further purification. Since the precursor is air and moisture sensitive, handlings of the precursors were carried out in a portable glove-bag under  $\text{N}_2$ . The precursor container was baked overnight in an oven before loaded in the glove-bag for the new charge of precursor. As soon as the container was attached to the CVD system, it was evacuated and kept at room temperature throughout the experiments without exposing to the air.

RBS was used to measure the thickness of each thin film. 2.0 MeV  $^4\text{He}^+$  ions were used in the Dynamitron ion accelerator at SUNY-Albany for the RBS measurements with a standard buried silicon detector. The backscattered spectra were collected with a beam spot of 20 mm<sup>2</sup>, a charge of 2–4  $\mu\text{C}$  and a current of 3 nA. The areal density of Co obtained from RBS was converted into an equivalent thickness by dividing it with the bulk atomic density of Co ( $9.04 \times 10^{22}$  atoms/cm<sup>3</sup>).

The surface chemistry of the four selected samples deposited at 70, 80, 140 and 160 °C were analyzed from spectra obtained by an X-ray photoelectron spectroscopy (XPS, Perkin-Elmer Co., USA) with a non-monochromatic Mg  $\text{K}_{\alpha}$  (1253.6 eV) source and a double-pass cylindrical mirror analyzer. The samples were loaded in an XPS chamber with a base pressure of  $1 \times 10^{-9}$  Torr through a loading dock. When the base pressure was reached, the samples at room temperature were then sputtered by Ar ions for 15 min. Ar gas with high purity was used for the sputtering process. A piece of blanket Co film of about

300 nm deposited in our e-beam system was served as a reference sample. This referencing sample was sputtered by Ar ions for 15 min in the same XPS chamber before the photoelectron spectra were taken. The peaks of interested elements found in XPS spectra were fitted using Origin 6.1 software, and the fitting parameters such as peak positions and widths were chosen manually with referring to the fitting results of the reference sample using Origin 6.1 software.

### 3. Results and discussion

We measured the deposition rate of Co CVD thin films using RBS. We plotted in Fig. 2 the deposition rate as a function of substrate temperature from 60 °C to 250 °C. A deposition temperature higher than 250 °C was not tested in this study due to the limitation of the highest temperature that our heater can provide. One deposition rate maximum was found at 120 °C and another maximum was found at around 220 °C if the rate continues to decrease after 250 °C. Between these two maxima, the deposition rate drops dramatically until it reached a minimum at 160 °C. One possible reason for the sharp increase of deposition rate around 120 °C is the increasing sticking coefficient of precursors at this low substrate temperature region [21]. When the substrate temperature was varied from 120 °C to 160 °C, although the sticking coefficient is still high, the precursor desorption increased as the temperature increases; hence, the growth rates decreased. The variation of the growth rate with temperature from 60 °C to 160 °C was believed to be the surface reaction controlled deposition. However, the growth behavior at the higher temperature regime from 160 °C to 250 °C may be considered as the diffusion-limited deposition [20]. The decomposition of  $\text{Co}_2(\text{CO})_8$

at low CO partial pressure environment has been proposed as [22–24]:



Reaction (1) follows a first order kinetics. The reverse reaction in (1) is believed to be very slow since CO is continuously being pumped away [23]. The decomposition of  $\text{Co}_2(\text{CO})_8$  to form  $\text{Co}_4(\text{CO})_{12}$  is believed to be a complex process with many possible pathways. The key to all of these pathways is the conversion of  $\text{Co}_2(\text{CO})_8$  to  $\text{Co}_2(\text{CO})_7$  by releasing one carbonyl ligand at low temperatures. Further decomposition is controlled by the mobility of the intermediates  $\text{Co}_2(\text{CO})_7$  on the surface, which can be dimerized to form  $\text{Co}_4(\text{CO})_{12}$  by releasing two more carbonyl ligands [23]. As we discussed in the Introduction, the growth behavior with two local maxima peaks was not reported yet. There is an inconsistency reported in the literature in terms of the substrate temperature at which the maximum growth rate is obtained. One reason of the difference can be that the different deposition pressures were used. Rhee et al. obtained the maximum growth rate at 200 °C in their CVD system with 50 mTorr deposition pressure [10]. Ko et al. reported that the temperature was 140 °C for their maximum growth rate at a 600 mTorr deposition pressure [14]. Greve et al. used an ultrahigh vacuum system to get the maximum growth rate at 175 °C [15]. And our deposition pressure was maintained at 10 mTorr. Since the precursor,  $\text{Co}_2(\text{CO})_8$ , is highly air and moisture sensitive, handle of the precursor and the treatment of substrates may affect the decompose behavior of the precursor. For example, if one treats the substrate using diluted HF, the substrate surface will be terminated with –OH and moisture will be introduced into the deposition system. We used dry  $\text{N}_2$  atmosphere during the handling to protect the precursor. New charge of precursor was used for deposition at different substrate temperatures.

We used XPS measurements to study the chemical quality of cobalt films deposited from  $\text{Co}_2(\text{CO})_8$ . The low-resolution spectra are shown in Fig. 3 after the surface oxide was sputtered away. The spectra from different deposition temperatures were obtained after 15 min of Ar sputtering. The rate of sputtering is estimated  $\sim 0.13$  nm/min from a calculation using the rate equation for sputtering [25]

$$Q_s(\text{atom/s}) = Y_s I_i / q_e, \quad (3)$$

where  $Y_s = 1.1$  is the sputtering yield of cobalt,  $I_i = 1.5 \times 10^{-5}$  A is the  $\text{Ar}^+$  ion current measured during experiment and  $q_e = 1.60 \times 10^{-19}$  C. The measured area of the sputtered spot was  $5.25 \times 10^{-4}$  m<sup>2</sup>. The carbon content is about 3% in the films. The Co 2p peaks were clearly shown in the XPS spectra after Ar sputtering of the sample surface. The original XPS spectrum of cobalt 2p line is a step-like curve with a higher intrinsic background of Co 2p<sub>1/2</sub> peaks than that of the Co 2p<sub>3/2</sub> peaks. The background thus was

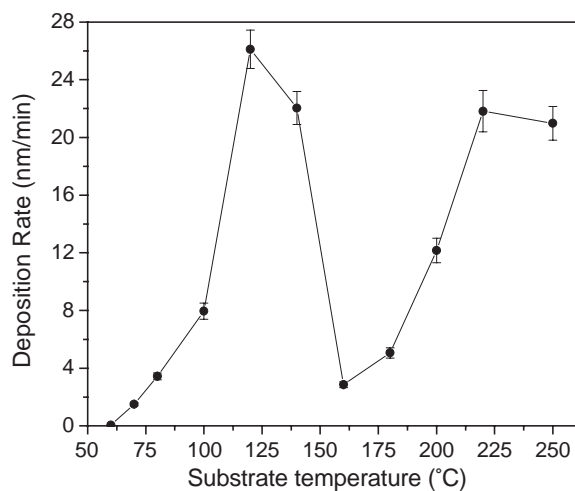


Fig. 2. Growth rates as a function of substrate temperature analyzed from RBS. Two peaks were found at 120 and 220 °C deposition temperatures.

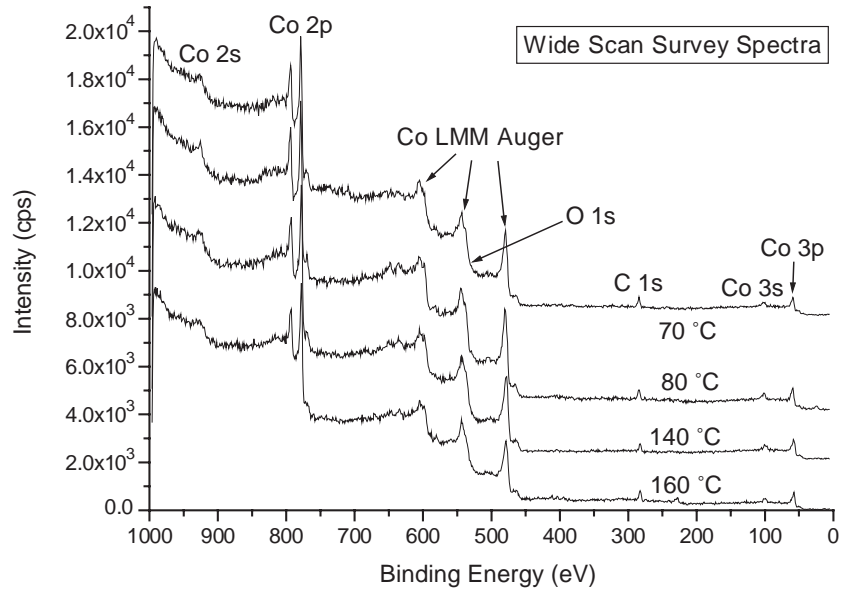


Fig. 3. Low-resolution scans of XPS spectra for Co films grown at 70, 80, 140 and 160 °C substrate temperatures after  $\text{Ar}^+$  sputtered for 15 min. The estimated rate of sputtering is  $\sim 0.13$  nm/min. The curves were shifted vertically for clarity.

subtracted from the data using Shirley model as discussed in the literature [26,27]. The Shirley background  $B(E)$  is defined as

$$B(E) = C \int_E^{\infty} [I(E') - B(E')]dE', \quad (4)$$

where  $C$  is a constant and is calculated through the iteration,  $E'$  is the binding energy and  $I(E')$  is the measured intensity

of the XPS spectrum at  $E'$ .  $B(E)$  was obtained using the iterative calculation and then was subtracted from the original data.

After the background subtraction, the Co peaks were presented in Fig. 4 from 805 eV to 765 eV range. Each peak was decomposed with the peak fit using a Gaussian model and the resultant fitted peaks are shown as dashed curves. We used the e-beam deposited Co film as a reference

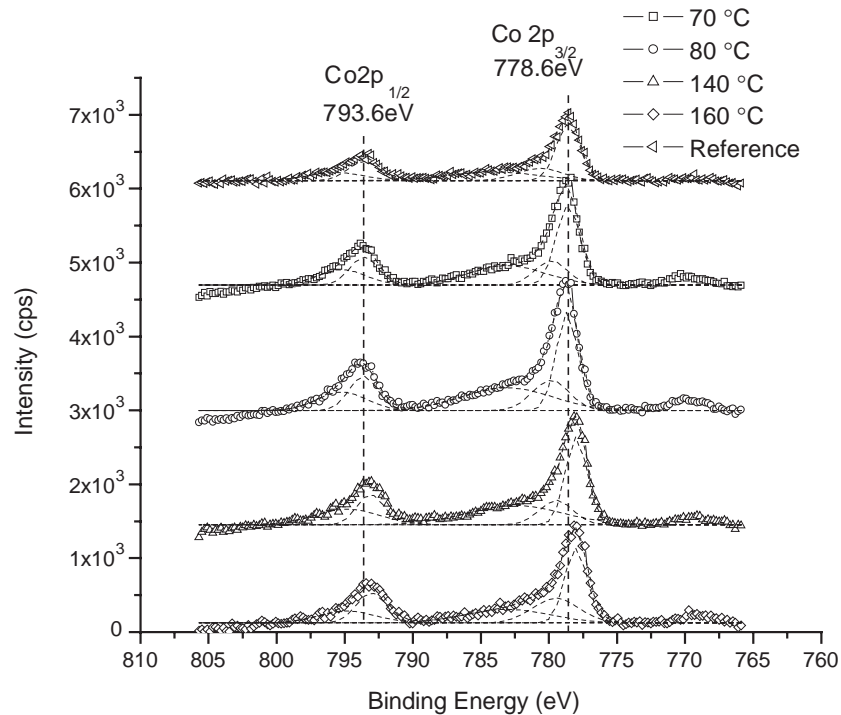


Fig. 4. XPS of Co spectra measured in the high-resolution scan mode from samples deposited at 70, 80, 140 and 160 °C substrate temperatures after  $\text{Ar}^+$  sputtered for 15 min. The estimated rate of sputtering is  $\sim 0.13$  nm/min. The curves were shifted vertically for clarity. The XPS spectra of e-beam deposited Co was placed on the top as a reference.

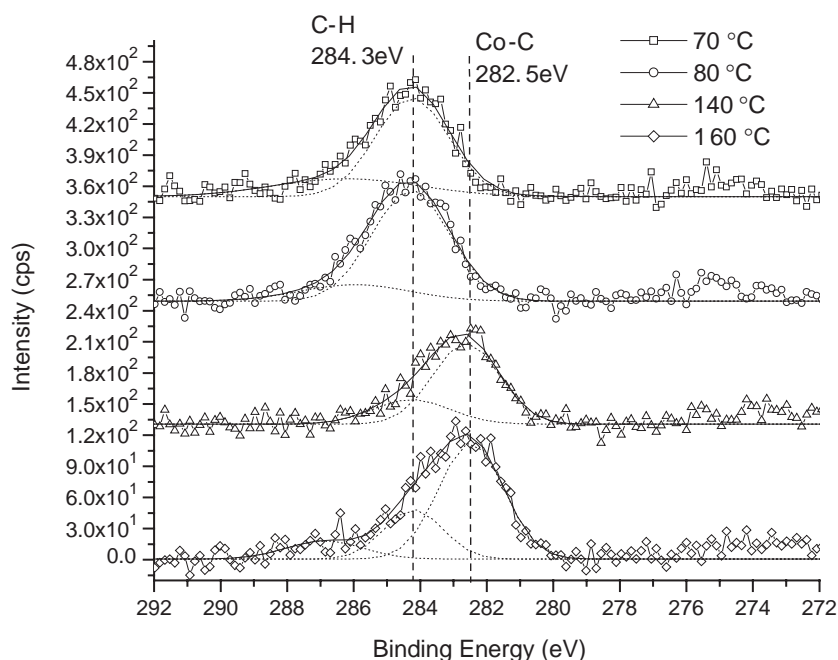


Fig. 5. Peak fit of high-resolution scans for carbon XPS peaks (C–H and Co–C) of four selected Co films deposited at 70, 80, 140 and 160 °C substrate temperatures after Ar<sup>+</sup> sputtered for 15 min. The estimated rate of sputtering is  $\sim 0.13$  nm/min. The curves were shifted vertically for clarity.

sample. The peak fitting parameters of our four CVD samples were determined from the fitting results of this reference sample. For the measured XPS spectra presented in Fig. 4, two common features can be seen: asymmetric line shape and a small bump around 770.2 eV. The asymmetric shape of Co 2p peaks is due to the interaction of X-ray induced core-hole and conduction electrons during XPS measurement [28,29]. We believe that the Mg  $\alpha_3$  X-ray satellite causes the small bump centered at 770.2 eV. The

displacement of this bump from the Co 2p<sub>3/2</sub> core level was measured as 8.4 eV. The relative intensity of the bump to the core level was measured as 10–12%. Both the displacement binding energy and the relative intensity are consistent with the literature [30]. For the samples prepared at 70 °C and 80 °C, the Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> peaks shown in Fig. 4 have binding energies of 778.6 eV and 793.6 eV, respectively. The Co peaks for the samples deposited at 140 °C and 160 °C shift to a lower binding energy or a higher kinetic energy

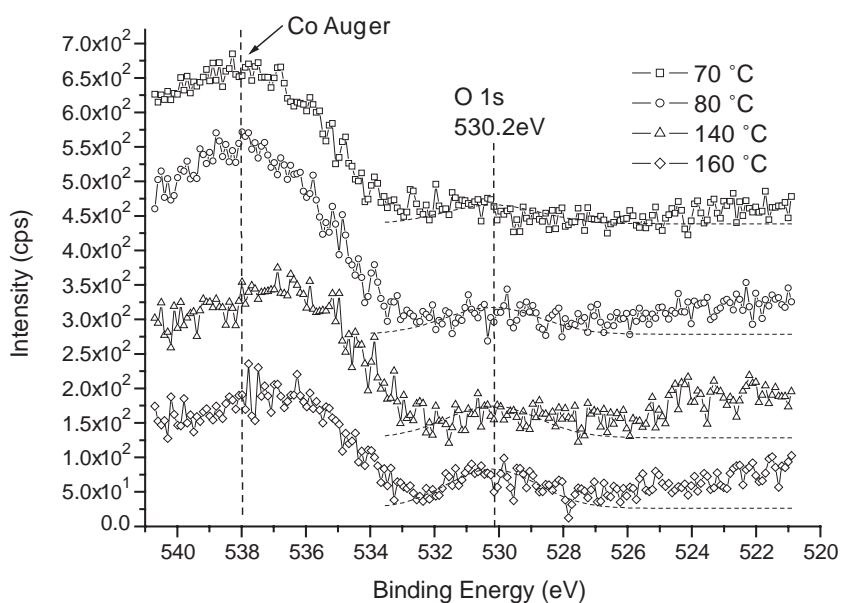


Fig. 6. Oxygen 1s peaks measured by XPS high-resolution scan mode from samples deposited at 70, 80, 140 and 160 °C substrate temperatures after Ar<sup>+</sup> sputtered for 15 min. The estimated rate of sputtering is  $\sim 0.13$  nm/min. An Auger LMM transition peak at 538 eV is indicated by the arrow. The curves were shifted vertically for clarity.

position by 0.6 eV. In vacuum decomposition at low temperatures, the precursor is adsorbed on surface intact [21] and the reaction (1) is limited. A complete reaction occurs to form metallic cobalt through reaction (2). Thus, the two major peaks of Co 2p in samples prepared at 70 °C and 80 °C have no chemical shift and are metallic Co films. However, the cobalt peaks in the samples deposited at 140 °C and 160 °C shift their positions to lower binding energy by about 0.6 eV suggesting that the cobalt is partially bonded to carbon in either of these samples. This argument is supported by the C 1s spectra as shown in Fig. 5 and explained next.

The high-resolution scanned C 1s spectra for the four selected samples after peak fit are shown in Fig. 5. Both spectra for the 140 °C and 160 °C samples show a peak at 282.5 eV, which is assigned to the carbidic carbon [31]. During the thermal decomposition of  $\text{Co}_2(\text{CO})_8$ , CO can be dissociated by cobalt at 140 °C and 160 °C deposition temperatures [32]. Thus, the carbon is formed through the disproportionation of chemisorbed CO over metallic cobalt throughout the deposited films. On the other hand, this process is very slow or prohibited at low deposition temperatures 70 °C and 80 °C. Consequently, there are only C–H bonds with the binding energy of 284.3 eV in both samples. To find out possible oxidation, the high-resolution scanned O 1s spectra for the four samples are shown in Fig. 6. The original spectra without processing show that O 1s peaks have step-like background intensity. This background intensity was subtracted using Shirley method as described above. The resultant intensity vs. binding energy from 521 to 541 eV is shown in Fig. 6. The O 1s peak at 530.2 eV is estimated to be about 2–2.5% at low deposition temperatures of 70 °C and 80 °C, and about 2–3% at 140 °C and 160 °C, from the area of O 1s peak in Fig. 6, and the total area of all the major XPS peaks emerged in the samples (Co 2p peaks, C 1s peak and O 1s peak).

#### 4. Conclusions

In this paper, we reported the deposition of cobalt thin films by CVD at low substrate temperatures (60 to 250 °C) via  $\text{Co}_2(\text{CO})_8$ . The deposition rate as a function of substrate temperature exhibits two maxima. The two-peak behavior is believed to be due to the change of sticking coefficient in the low temperature region studied. The cobalt thin films deposited at 70 °C and 80 °C were predominately metallic from XPS measurements and analysis. Our XPS spectra of C 1s in the samples prepared at higher temperatures 140 °C and 160 °C suggested that cobalt carbide was formed as a result of CO disproportionation by cobalt. Carbon contamination is minimal in the bulk of the films and the oxygen contamination is extremely small. These CVD cobalt thin films deposited at a low temperature are competitive with CVD cobalt films deposited by other precursors.

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