

## Valence band density of states of small cobalt particles on Si(111) substrate

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Received 18 May 1993; accepted 4 April 1994

Small Co particles were prepared by sputter etching of a 4–5 nm thick “island-like” Co film deposited on Si(111) substrate. The density of states (DOS) of the valence band was measured by means of ultraviolet photoemission (UPS) during the sputter etching to monitor the formation of small Co particles. It was found that at a given thickness of the Co island the Fermi level was shifted by 1.8–1.9 eV toward higher binding energy and the DOS decreased or no states were detectable at the Fermi level. This effect was explained by the formation of small Co particles with electronic structure which is significantly different from that of the bulk Co.

**Keywords:** small Co particles; photoemission; DOS

### 1. Introduction

Modelling the highly dispersed metal catalysts by using the well controlled thin film technique may help us to correlate electron properties to catalysis. The morphology and electron properties of particles with near atomic sizes may significantly differ from those of bulk materials. Some efforts which were spent to obtain deeper insight into the structure of these “quantum dots” for semiconductors and quantum clusters for metals, were reported earlier [1].

Preparation of these extremely small size particles needs highly sophisticated techniques such as MBE, electron ion lithography and deposition via quadrupole mass spectrometer [2–4]. Earlier methods to prepare discontinuous films that had served as a model, were hampered because of very low reproducibility. A combina-

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tion of the thin film deposition technique along with sputter etching seems to be a promising method to prepare small particles provided that the “as-deposited” film is an island-like one, because in this case one can assume that the sputter etching process will decrease the sizes of the islands in three dimensions.

Correlation between sizes and DOS of the valence band has been investigated only for atomic clusters [5–8]. It is, therefore, highly probable that DOS of the Co valence band will be changed as the dimensions of the islands approach the near atomic dimensions.

In the present work the Co film deposited on a Si(111) single crystal substrate will be investigated at room temperature. It is also expected that the electronic state originated from Si 3p, will not interfere with the Co 3d states.

## 2. Experimental

The cobalt film was deposited onto a Si(111) wafer substrate, that was annealed first at 1070 K for 3 min, in an oil free vacuum system (Varian VT-460). The Co thin layer was evaporated by an electron gun operated at 2–400 W power and the substrate was at room temperature during the deposition. The thickness of the layer was measured by means of vibrating quartz and on average it amounted to 4–5 nm. As a reference a 100 nm thick Co/Si(111) sample was applied.

The deposited layer was loaded to an electron spectrometer (Kratos ES-300) for UPS and XPS measurements. The sample was ion bombarded using an Ar ion gun working at 0.5–2 keV energy.

The incidence angle of the Ar ion was 30° with respect to the normal of the Si(111) surface. The etching process was monitored by UPS technique, which simultaneously served to determine the DOS of the valence band of the thick Co film with bulk-like properties, of that of the small Co particles formed and finally of the Si substrate after complete removal of the Co layer. For UPS a He(I) or Mg  $K_{\alpha}$  source was applied. Contamination and the 2p core level bands for Co and Si were measured by XPS using Mg  $K_{\alpha}$  excitation.

After deposition and after sputter thinning the samples were measured by TEM with replica technique.

CoSi and CoSi<sub>2</sub> were prepared by heating the Co/Si(111) samples in argon for 30 min up to 770 and 1270 K, respectively. Here, cobalt silicides are formed in a 40–50 nm layer. The structures were identified by XRD using a Philips X-ray diffraction apparatus equipped with a Guinier chamber.

## 3. Results

The He(I) ultraviolet spectrum for the 100 nm thick Co film after surface cleaning is presented in fig. 1 (curve a). The intensity of the DOS at the Fermi level  $N(E_F)$  is very high and a maximum is observed at 0.6 eV binding energy. The width

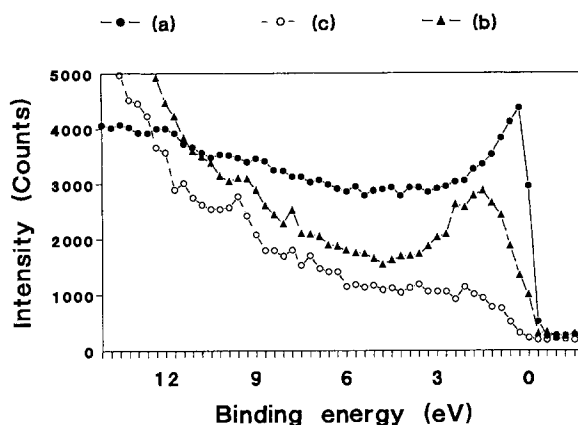


Fig. 1. UPS spectra for 100 nm thick Co/Si(111) film (curve a) for thinned 4–5 nm Co/Si(111) film after ion etching (curve b) and for the clean silicon substrate after removing the Co layer by in situ sputtering (curve c). The photoemission data were obtained by He(I) excitation.

of the DOS is about 4 eV. This result is in agreement with other experimental data [9] and theoretical calculations [10]. This spectrum can be regarded as reference with respect to the further changes caused by sputter etching. The same spectrum was obtained for the “as-deposited” 4–5 nm Co film.

Curve b in fig. 1 shows the UP spectrum of the 3.5 nm Co/Si(111) film after etching by Ar ions for 30 min. A visible decrease in the intensity at the Fermi level and the shift of the band maximum towards higher binding energy (about 2 eV) are indicative of the changes in the structure of the Co thin layer. The peaks appearing in the 6–10 eV binding energy range can be assigned to the Si substrate and to the 3p valence level of the Ar ions embedded during the ion bombardment. These features are also observed in the spectrum after the complete removal of the Co layer as demonstrated by curve c in fig. 1.

In fig. 2 the spectra represented by the curves a, b and c for the 100 nm thick Co film, for the sputter etched Co film and the Si after complete removal of the Co film, respectively, were measured using Mg  $K_{\alpha}$  excitation. Curve a shows that the band for the Co layer has a width of about 4 eV along with a maximum at 0.6 eV binding energy and this agrees with the UPS data. Curve b, representing the UP spectrum of the sputtered 3.5 nm Co layer, indicates a shift of the maximum towards 2.0 eV and the binding energy at 8–10 eV is originated from Si. Curve c shows the valence band spectrum for the pure Si substrate with the contribution from the small Co particles similarly to the UPS data.

In the spectrum shown in fig. 2 the electron states originated from Co 3d and Si 3p are overlapped. Although this fact may disturb our UPS data in the 0–4 eV energy range, the shape of the Si 3p band, however, is different from that representing Co 3d, as well as its intensity is also much smaller than that observed for Co 3d in the spectrum shown by curve b. The difference curve between b and c in the

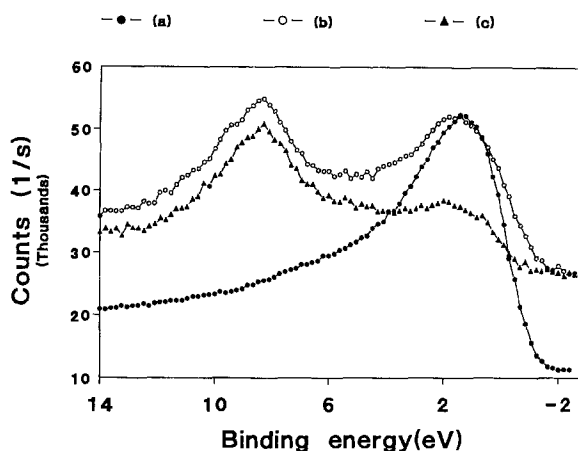


Fig. 2. Valence band results for the same samples as given on fig. 1 using Mg K $\alpha$  excitation.

0–5 eV range can be correlated mostly with the Co 3d states and this is rather different from the DOS measured for thick Co layer (see fig. 3).

The Co 2p $_{3/2}$  core level band of the sputtered etched sample is given in fig. 4. It is seen that this level is shifted towards higher binding energy by 0.5 eV (778.4 eV instead of 777.9 eV given for bulk cobalt [11]).

The structure–electron density relationship indicated above can be observed by two facts. After Ar ion sputtering the shift in the Co 3d level toward higher binding energies might be ascribed either to cobalt silicide formation or to charging effect.

Although Co silicide might already be produced at near room temperature on a very thin film of Co [12], high temperature is required for the formation of a well defined silicide structure at thermal and rapid thermal annealing [13–15]. Our CoSi

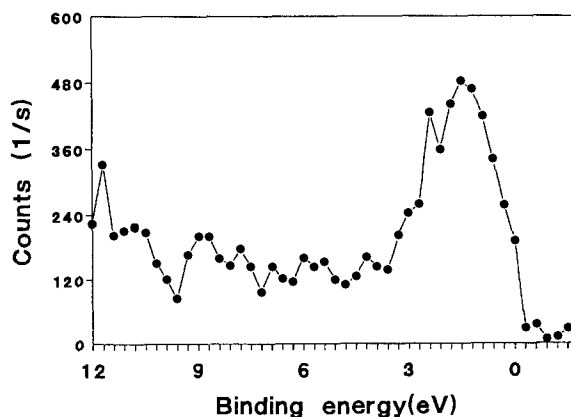


Fig. 3. The valence band density of states of small Co particles obtained by subtraction of curve c from curve b (subtraction of the Si substrate originated emission) shown in fig. 2.

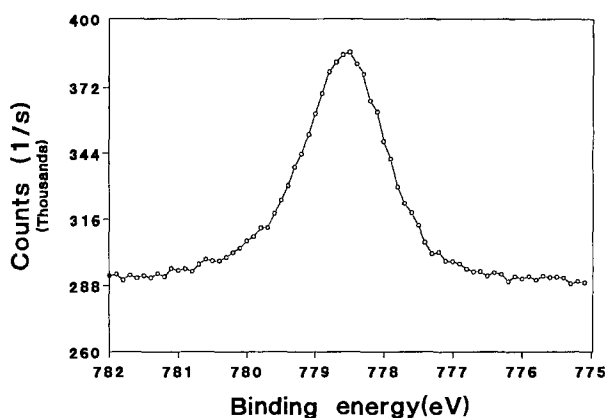


Fig. 4. The cobalt  $2p_{3/2}$  core level XPS spectrum for the Co/Si(111) samples after sputtering.

and  $\text{CoSi}_2$  samples were characterized by XRD. The diffraction lines for CoSi are at 0.312, 0.256, 0.198, 0.182, 0.117, 0.1045 and 0.1014 nm, which are indicative of polycrystalline CoSi. Similarly for  $\text{CoSi}_2$  XRD lines at 0.188 and 0.138 nm for 220 and 400 faces, respectively, were measured, which corresponds to  $\text{CoSi}_2$  single crystal. In figs. 5a and 5b the UPS curves are presented for CoSi and  $\text{CoSi}_2$  samples, respectively, with well developed structures. If one compares these curves with curve a in fig. 1, the difference is negligible. Consequently, Co silicides cannot have played a significant role in the shape of curves b in figs. 1 and 2.

In order to estimate to what extent the binding energy shift observed on small, isolated metal particles is caused by a charging effect, a Si(111)/ $\text{SiO}_2$ /Co layer (4–5 nm Co) was prepared. Here, after sputter etching, small Co particles are not in contact with the Si(111) substrate. After long time UV irradiation a complete absence of the valence band at Fermi level is observed shown in fig. 6 (curve a) as a result of charging. However, the Co 3d band is resumed after the particles have discharged (curve b) via the leakage through the distance between the Co–Co.

The morphology of the “as-deposited” and the sputtered 4–5 nm Co/Si(111) samples is attempted to measure by the TEM replica presented in figs. 7 and 8, respectively. The TEM data shows that the as-deposited sample consists of islands of around lateral size of 80–100 nm diameter. On the other hand, the sputter etched sample has grains of lateral size of around 10 nm.

#### 4. Discussion

For the 100 nm Co/Si(111) cobalt film the DOS of the valence band being identical with that obtained for the bulk states [16], is characterized by a maximum at 0.6 eV binding energy and high intensity at the Fermi level (curves a in figs. 1 and 2).

No emission can be assigned to the Si(111) substrate (Si 3p) or to other sources

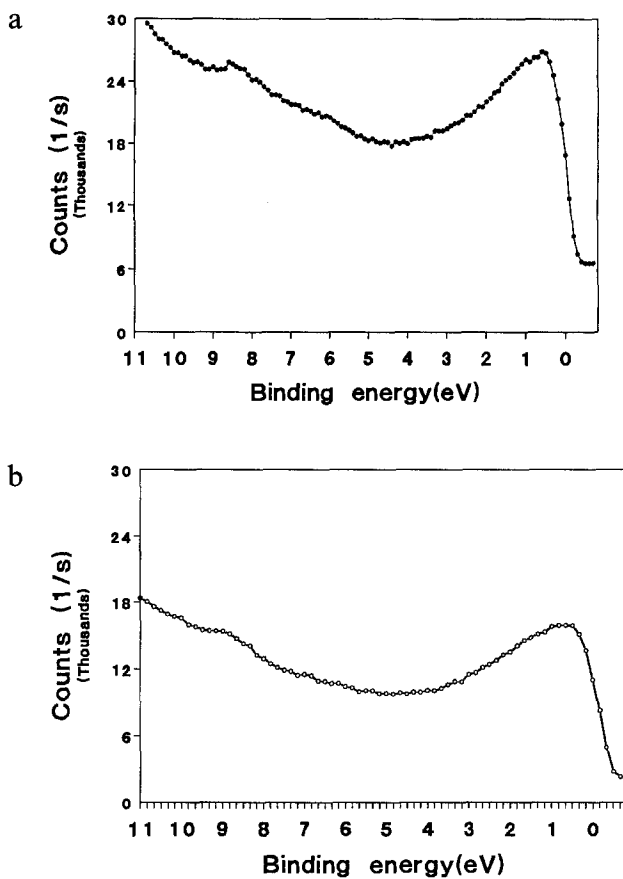


Fig. 5. UPS spectra of CoSi (a) and CoSi<sub>2</sub> (b) samples.

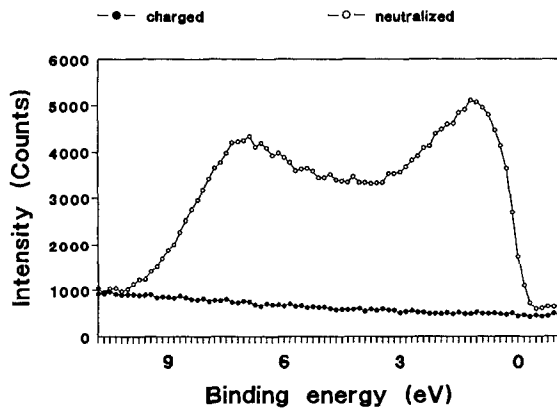


Fig. 6. UPS spectra for Co/SiO<sub>2</sub>/Si(111) charged by UV irradiation (charged), and the discharged sample (neutralized).

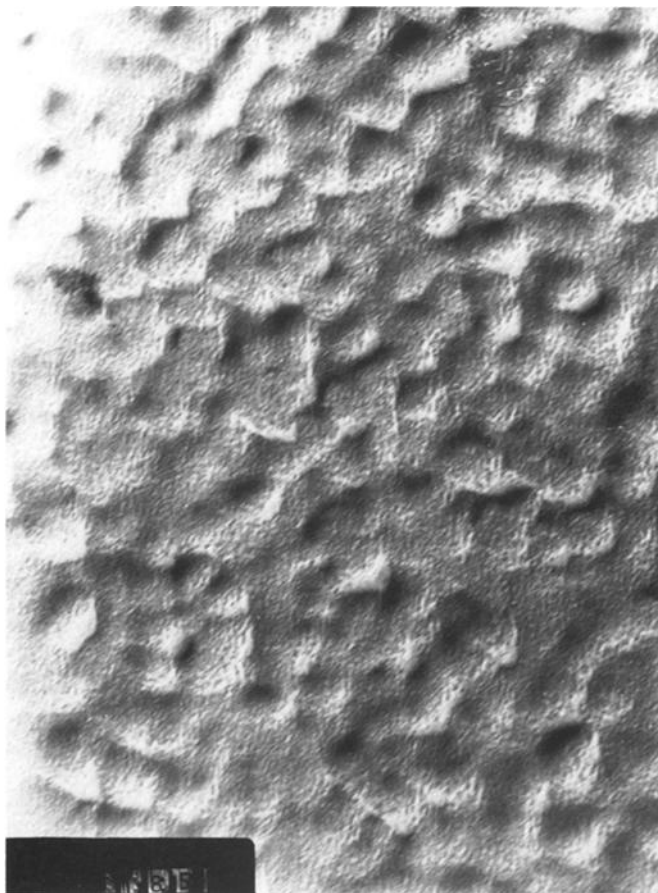


Fig. 7. TEM replica picture obtained from the “as-deposited” cobalt film. The magnification is 75000.

like O 2p, C 2p or Ar 3p, thus, according to the sensitivity level of the photoemission, the Si(111) substrate is fully covered with cobalt. Moreover, this cobalt layer is at least 2 or 3 times thicker than the escape depth of the excited photoelectrons.

After a sufficient sputter etching of the 3.5 nm Co/Si(111) sample the UPS and XPS data given by curve b in figs. 1 and 2 can be regarded as the sum of the emissions originated from Co 3d, Si 3p, Ar 3p, Si(s + p) and O 2p or C 2p states.

To clarify the possible sources of Si, Ar, Co, O, C the Si(111) substrate was measured after removing the cobalt from its surface (curves c in figs. 1 and 2). It seems that change in the valence band is allocated only in the 0–5 eV binding energy range. At higher binding energy only the band intensity increased as a result of the increasing fraction of the substrate exposed to the surface, once the cobalt had been removed. The difference spectrum between the curves b and c in fig. 1 given in fig. 3, can be regarded as the DOS for Co 3d of the thinned Co film.



Fig. 8. TEM replica picture from the thinned sample given by curves b in figs. 1 and 2. Magnification is 75000.

It appears that the 3d states of the thinned cobalt film are very much restructured compared to that of the thick cobalt deposits. The DOS at Fermi level is not detectable at the sensitivity level of the UPS and the maximum of the 3d states is shifted to higher binding energy (0.6 eV to 1.8–2 eV for transition of “as-deposited” 4–5 nm Co film to small Co particles, respectively).

The lack of the Fermi edge, i.e. the decrease in the DOS intensity and the shift of the Co 3d maximum is well observable for the Co valence band, can be interpreted by the Co islands of nm size after the sputter etching process and the TEM replica pictures do not contradict with this statement.

The possible explanation is that during sputter etching the size of island decreases in all dimensions mostly via a geometrical effect. Nevertheless, the lateral dimension (around 10 nm) does not change DOS too much and the drastic change can be ascribed to the decrease of the size along the axis normal to the surface, i.e. the formation of a “raft-like” surface geometry.



However, the charging effect and the interaction between Si and Co forming Co silicide, can also be encountered as possible artifacts.

The possibility of the charging effect may be excluded by comparing the electron band structure with and without artificial UV charging (see fig. 6). In addition, the behavior of the Co  $2p_{3/2}$  core level spectrum of the sputter etched sample (fig. 4) indicates only a 0.5 eV shift towards higher binding energy. This is significantly smaller than the 1.4 eV shift of the 3d maximum measured in the valence band. Nevertheless, the core level shift of the small Co particles is an indication of the charge transfer which results in an electron deficient  $\text{Co}^{\delta+}$  formation which is characteristic of small particles [17,18].

The absence of charging can also be supported by a comparison of the present results with the data measured for Ga islands on GaAs substrate. This indicates that the observed charging effect shown by the shift at the Fermi level was the same as the shift at the core level of Ga [19]. This also supports the lack of charging effect here.

The possibility of the formation of Co-silicide compounds can also be excluded on the basis of the DOS data measured for CoSi and  $\text{CoSi}_2$  (fig. 5). The spectra are essentially the same as that for Co/Si(111) except some broadening at the 3d states and 0.2 eV shift of Co 2p states. Comparing the DOS data for Co-silicide compound with that for the small Co particle it is seen that they are markedly different and one can exclude the Si 3p and Co 3d hybridization as the source of the experimental data observed for the small Co particle.

Direct correlation of our experimental data with other theoretical or experimental results is not possible because of the lack of the available data. However, it was shown that the ionization potential in alkali atom clusters is larger than the work function, only for those having around 100 atoms (bulk-like structure). Here the size is probably very much smaller than number in our case [5–7].

The geometry of the small Co particles is similar to semiconductor quantum dots (10 nm diameter, 1–2 nm thickness) rather than to clusters. This is why the number of Co atoms larger than 100 and the drastic change in DOS in these particles may not be in contradiction with the data given for clusters.

## 5. Conclusion

It was established that sputter etching of an “island-like” film is a suitable process to prepare small non-interacting particles in nm dimensions that serve as a model for highly dispersed catalysts. The Co 3d photoemission characteristics originated from bulk cobalt cannot be scaled down to Co islands with nm sizes. Instead, the Co 3d emission can be assigned to a modified valence band density of states of the small Co particles compared to the bulk material. This is characterized by a shift in the maximum of the d-states towards 1.8–2 eV binding energy and by the large intensity decrease. The lack of the states at Fermi level in the sensitivity

range of the photoemission technique is also an excellent indication for the change in the electron properties of the particles in nanostructure scale.

This large modification of the valence band density of states of cobalt can be only understood if one assumes the existence of particles with near atomic size. This system may be regarded as assembly of small structureless metal clusters.

Other phenomena such as charging, chemical interaction which can also be the source of the experimental observations of small Co particles on silicon substrate, could be excluded by direct experimental evidences.

## Acknowledgement

The authors are indebted to Z.F. Horváth for the TEM measurements and to E. Zsoldos for the XRD data. The financial support of the National Science and Research Found (Grant No. 296331887) and of the Surface Science Programme co-sponsored by the National Committee for Technical Development and the Hungarian Academy of Sciences is greatly acknowledged.

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