

- "Theory of Orientation and Stereoselection" Springer-Verlag, Berlin, 1975.
12. R. A. Y. Jones, "Physical and Mechanistic Organic Chemistry," 2nd ed., Cambridge Univ. Press, London, 1984, p. 134.
 13. The MNDO method used in this work does not include *d*-orbital for S-atom so that calculations involving hypervalent S-compound are reported to have some inconsistencies. However the species V has octet electrons, although it appears to have hypervalent, so that the use of basis sets without *d*-orbital for S cause no problem M. J. S. Dewar and C. H. Reynolds, *J. Comput. Chem.*, **7**, 140 (1986).
 14. J. Catalan and M. Yanez, *J. Chem. Soc. Perkin Trans. 2*, 1627 (1979).

Passive Film on Cobalt: A Three-Parameter Ellipsometry Study During the Film Formation

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Thin film being formed on the surface of cobalt in the early stage of electrochemically induced passivation was studied by the three-parameter ellipsometry. The growth of the passive film was complete in a few seconds from the onset of the passivating potential, and was followed by a slight decrease in the thickness in 4-40 seconds. The optical constants of the passive film changed gradually during the changes in the thickness. The thickness and the optical properties at the steady state of passivation depended on the potential of the electrode. From the coulometric data and the optical properties, the composition of the passive films was deduced to be close to those of CoO, Co₃O₄, and Co₂O₃ depending on the potential. Cathodic reduction in the presence of EDTA was found to be an efficient way to obtain film-free reference surface of cobalt.

Introduction

Surface films formed with passivation of cobalt have been studied by spectroscopic methods,^{1,2} electrochemical measurements,³ the conventional (two-parameter) ellipsometry combined with electrochemical methods,⁴⁻⁷ and briefly by the three-parameter ellipsometry.⁸ The three-parameter ellipsometry has also been used to study surface films on various metals in number of laboratories.⁸⁻¹⁵ The method, also called combined ellipsometry-reflectance technique because reflectance change is measured in addition to the usual Δ and Ψ measurements of ellipsometry, proved to be particularly useful for monitoring the changes in passivating layers on iron and nickel electrodes in early stages of the layer formation.¹⁶⁻¹⁸ The earlier study on cobalt using the three-parameter ellipsometry method for the first time^{8,14} was mainly to test the feasibility of applying the method for determining the thickness and optical properties of thin films having complex refractive indices, and the method has not been applied to its full advantage for the study of passivation of cobalt.

The present study was conducted in order to study passive film on cobalt, particularly the nature of the passive film during its formation stages, by auto-recording three-parameter ellipsometry. The variations of the optical properties and the thickness of the passive films being formed on cobalt surface were determined in 0.1s to 100s after the potential of the cobalt electrode was stepped to a passivating

potential. The optical and electrochemical measurements were made simultaneously to deduce the approximate composition and properties of the passive film. The results are presented here.

Experimental

Materials. Cobalt electrodes were prepared by vacuum deposition of thermally evaporated 99.99% cobalt on glass slides to approximately 1 μm thickness. A thin layer of chromium was first deposited on the glass slide before the cobalt deposition to make the cobalt film more adhering. A buffer solution of 0.08 *M* sodium borate-0.35 *M* boric acid, pH 8.65, was used as the electrolyte solution. The solutions were prepared from reagent grade chemicals and doubly distilled water of specific resistivity greater than 10 *M* ohm-cm. To remove the fine particles suspended in the prepared solution, which scatter the laser light of the ellipsometer and hence cause noises in the optical measurements, a membrane filter of 0.45 μm pore size (Millipore HAWP-04700) was used prior to the transfer of the solutions into the cell.

Equipment and Measurements. An automatic ellipsometer built in this laboratory was used in the present study. The ellipsometer is equipped with a He-Ne laser of 632.8 nm wavelength as the light source and is capable of recording the reflectance (*R*) change as well as the changes in the usual ellipsometry measurements Δ and ψ as described previously.^{16,18} The cobalt electrode was mounted in an electrochemical-optical cell. The cell had a Pt counter elec-

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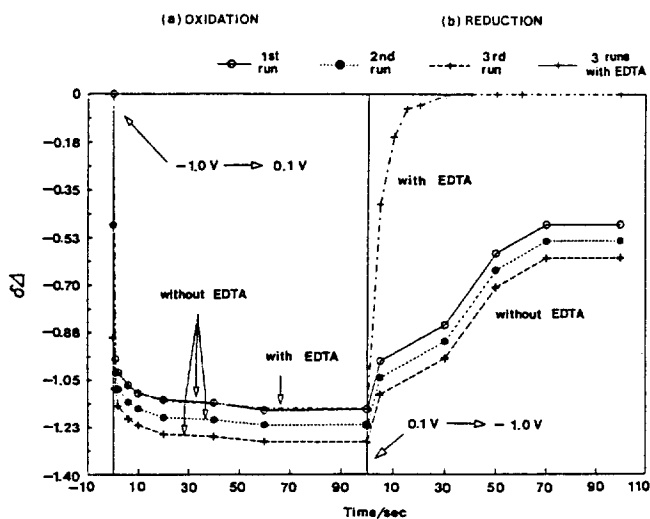


Figure 1. Changes in the ellipsometric Δ during three consecutive cycles of potentiostatic oxidation-reduction in the presence of EDTA (—); during a cycle in the absence of EDTA (---).

trode, a saturated calomel reference electrode connected to a Luggin probe, and optical windows made of fused quartz. The angle of incidence, whose proper choice for each system under study is essential for a successful applications of the three-parameter ellipsometry,^{14,18} was fixed at 55° in the present work. The solution was deaerated by bubbling of purified nitrogen prior to measurements.

The cobalt working electrode was initially maintained at a reducing potential near -1.0 V *vs.* SCE to ensure a film-free reference surface before inducing film formation by potentiostatic oxidation, using an EG & G PAR model 173 potentiostat whose rise-time is 1 μ s. Simultaneous ellipsometry measurements were started on the electrode surface. The potential was then stepped from -1.0 V to various oxidizing potentials in the range -0.1 to $+0.35$ V to start formation of the passive film, and the concomitant optical signals of Δ , Ψ and R were recorded by a multichannel oscillographic recorder. To repeat the measurement, the surface must be reduced to the film-free state at a cathodic potential before next application of the passivating potential. For this purpose, disodium salt of ethylenediaminetetraacetic acid (EDTA) was introduced into the buffer solution to the concentration of 0.1 M. Metals such as iron, nickel, and cobalt present a problem of residual surface films that remain even at reducing potentials. Thus, once the metals have been subject to an oxidizing potential, the ellipsometric readings do not completely return to the original readings on bringing the potential to moderately reducing potentials. Therefore, it is not usually possible to obtain a film-free optical reference state and at the same time to avoid application of an excessively cathodic potential which can cause hydrogen evolution. It is also impossible for the same reason to repeat the oxidation and reduction experiments on a single sample surface. Smialowska *et al.*^{19,20} showed in their study of iron passivation that in the presence of EDTA, the ellipsometric readings of Δ and Ψ could be brought back to the original values of the film-free iron surface after each of the repeated oxidation and reduction cycles, indicating that complete removal of the surface film was achieved. Application of EDTA was at-

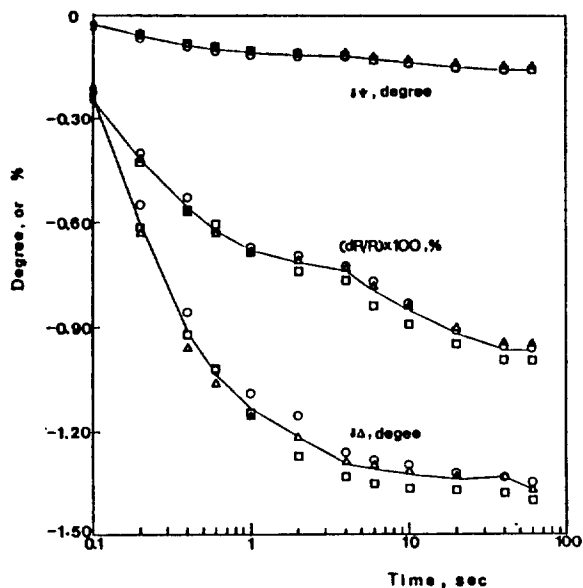


Figure 2. Typical changes in Δ , Ψ and R after the potential step from -1.0 V to 0.2 V *vs.* SCE. The wavelength: 632.8 nm. Angle of incidence: 55° . The different markers are for individual runs of repeated experiments. The lines represent the average values.

tempted in the present study to see if it also is effective for removal of surface film on cobalt. As a result, it was found that the cobalt surface can be reduced repeatedly to the film-free reference state as can be seen from the reversible changes in Δ on oxidation and reduction with EDTA shown in Figure 1, in contrast to the case without EDTA. The changes in Ψ also behaved in a similarly reversible manner. The oxide or hydroxide species in lower oxidation states that usually remain on the surface after the cathodic treatments are completely removed perhaps by dissolution with the help of ligand action of EDTA. The presence of EDTA did not affect the passive film formed as indicated by the closeness of the optical signals obtained in the presence of EDTA to those obtained in the first oxidation without EDTA. The applied potentials were limited to below 0.4 V *vs.* SCE to avoid roughening of the surface. This range of the applied potential is deemed relevant to the study of passivation that may occur in the ordinary environment.

Results and Discussion

The optical constants of the vacuum-deposited cobalt, n and k of the complex refractive index ($\tilde{n} = n - ik$), were calculated to be 2.34 and 4.18, respectively, from the ellipsometric readings on the film-free surface at the wavelength of 632.8 nm. These values are in close agreement with those estimated from the values at near-by wavelengths in the literature,^{7,8,21} and were used in the subsequent calculations of thickness and the optical constants of the films forming on this substrate.

Recordings of the ellipsometric parameters Δ , Ψ and R were made from the moment when the electrode potential was stepped from the reducing potential to a passivating potential. A typical result of such a recording is presented in Figure 2. From these three recorded parameters, thick-

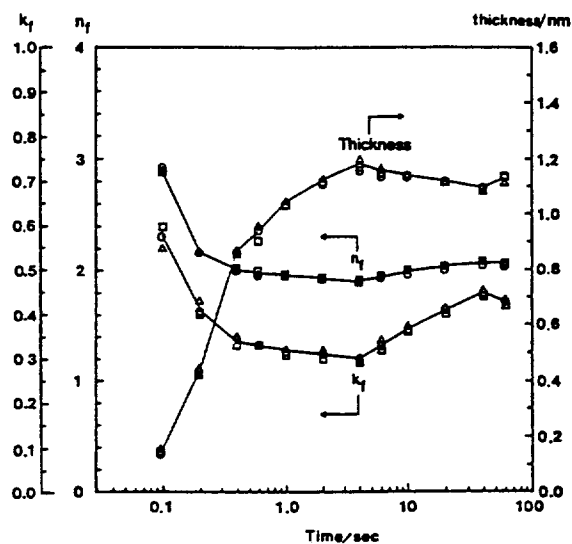


Figure 3. Changes in thickness, n_f , and k_f (for the wavelength of 632.8 nm) of the film formed on the cobalt surface after the potential was stepped from -1.0 V to 0.1 V vs. SCE. The different markers are calculated results from individual runs of the repeated experiments. The lines represent the average values.

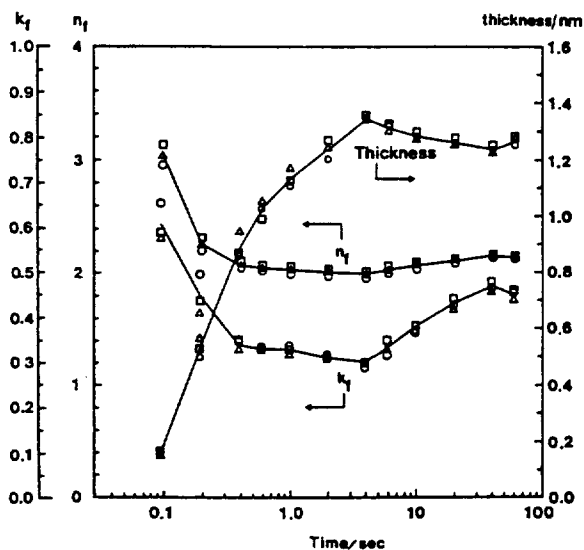


Figure 4. Same as in Figure 3, but with potential step to 0.2 V.

ness and optical constant (n_f and k_f of the complex refractive index $\tilde{n} = n_f - ik_f$) of the film forming on the cobalt electrode were calculated, as functions of time elapsed after the onset of the passivating potential. For the calculation, a homogeneous film between the metal and the solution was assumed and a numerical solution of the three-parameter ellipsometric equations was sought by iteration. At least three runs of experiments and the calculations for each run were repeated at each passivating potential. Unique numerical solutions were obtained for most of the repeated experiments. The results are shown in Figures 3, 4, and 5, for three different passivating potentials of 0.10 , 0.20 , and 0.3 V vs. SCE. A general feature common to Figures 3, 4, and 5 is that the thickness of the films reaches a value near 1.2 - 1.4 nm in

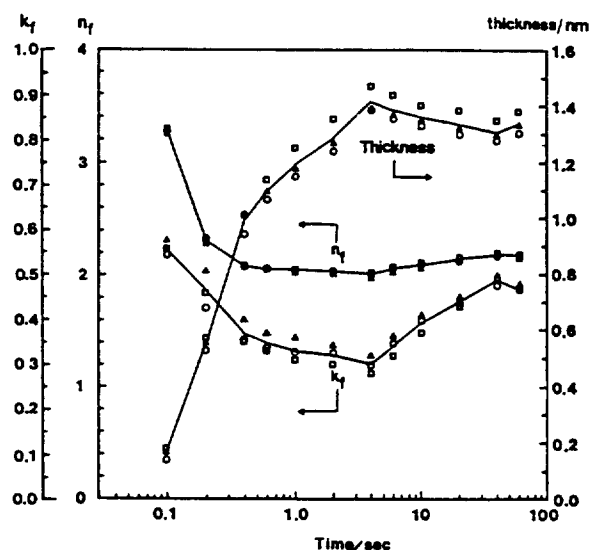


Figure 5. Same as in Figure 3, but with potential step to 0.3 V.

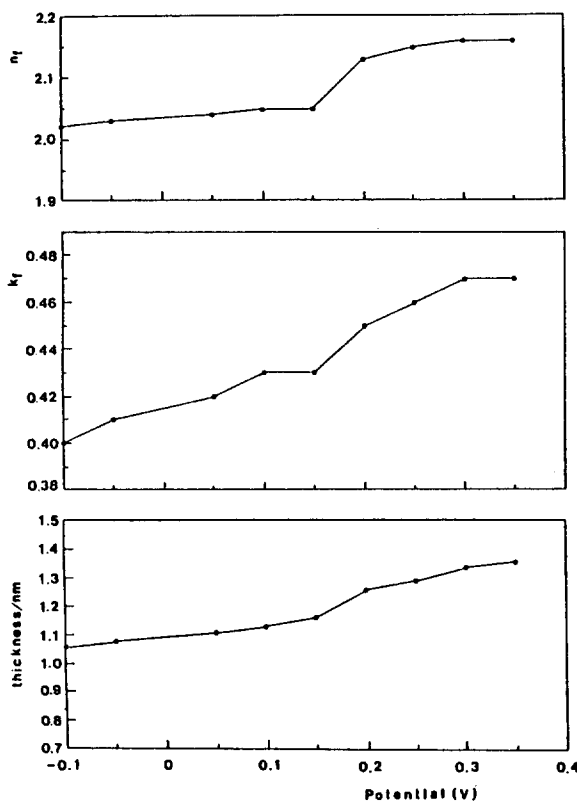


Figure 6. Thickness and optical constants of the films after reaching steady states at various anodic potentials.

3 - 4 seconds, then it relaxes one or two tenths of a nanometer before it approaches a near-steady state value after about a minute. The n_f and k_f values exhibit slight dips at the time when the thickness is at the small peak, the variations in n_f and k_f being almost symmetric to that of the thickness. The slight decrease in the thickness accompanying the slight increases in the values of n_f and k_f is considered to indicate a structural reorganization, perhaps loss of hydration water from the oxide species of cobalt. The initial (≤ 0.4 s) big

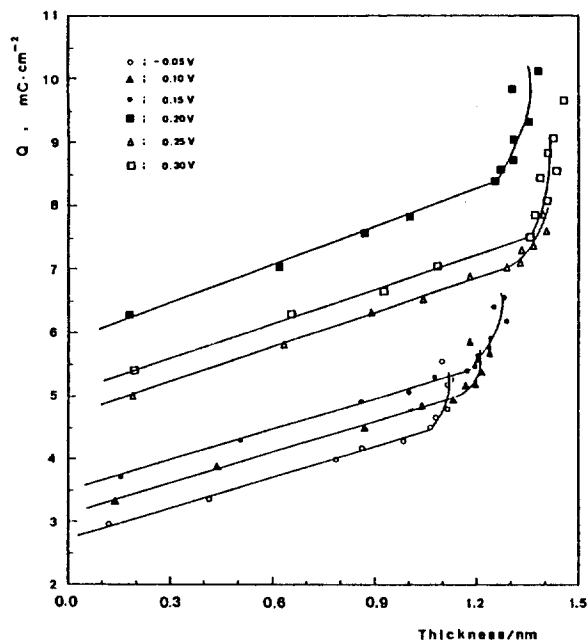


Figure 7. Oxidation charge values expended during the formation of the anodic films formed at various potentials *vs.* the thickness determined by ellipsometry.

drops in n_f and k_f may be due to transformation of submonolayer or patchy oxide islets to a continuous multilayer structure.

Figure 6 shows the thickness, n_f and k_f values of the passive films after about 100 s at potentials in the passive range when the system reaches a quasi-steady state. Roughly, three different potential regions can be identified: between -0.10 and 0.15 V where thickness and n_f remain at relatively low values; between 0.15 and 0.25 V where both the thickness and the optical constants (especially n_f) increase sharply with increasing anodic potential; and between 0.25 and 0.35 V where both the thickness and the optical constants do not vary significantly with the potential. The real part of the optical constants of the passive films n_f is smaller than those of CoO ($2.4-i0.1$), Co_3O_4 ($3.2-i0.5$), and Co_2O_3 ($3.2-i0.95$) reported by Sato, *et al.*,^{5,7} and also than those of CoO ($2.6-i0.4$) reported by Paik and Bockris⁸ and by Powell and Spicer.²² The imaginary part k_f is within the reported range. All these literature data are results measured at wavelengths somewhat different from that used in the present work. Cook, *et al.*²³ obtained by the Kramers-Krönig transform, n_f as a function of photon energy, and their n_f value for the present wavelength is only slightly greater (~ 2.2) than the present value. Any change in k_f may reflect small deviations

from the stoichiometry of the oxide or a minor change in the coordination among the ions in the thin layer,²³ and hence should not be given a weight in considering the identity of the film materials. In Figure 7, coulometric anodic charges expended during the formation and growth of the passive films are plotted against the instantaneous film thickness calculated from the ellipsometry data. Except at the upper ends of the curves where the currents are used mostly for parasitic or partial dissolution reactions after the films have approached full thickness, the charge to thickness relations reflected by 4 to 7 experimental points are remarkably linear. This seems to indicate that the stoichiometric composition of a film does not change during the film formation stage at a constant potential. The slopes of the lines, $dQ/d\tau$, however, for different potential ranges, are different and are summarized in Table 1, along with theoretical $dQ/d\tau$ values calculated for some of the oxides of cobalt with known densities. The experimentally determined $dQ/d\tau$ values in the three different potential ranges can be matched respectively with the theoretical values for the three known oxides in the next column of the Table 1.

It can be noted that the thickness and the optical constants, especially the n_f value, do not show wide variations within each of the three potential ranges except at near 0.2 V, while the variations between the ranges are substantial. Therefore, the compositions of the passivating films appear to be close to the known oxides in the "calculated" column, even at these extremely thin thicknesses where it is hard to expect a phase of definite stoichiometry. Thus, the film formed at lower passivation potentials (below 0.15 V) is close to CoO; at potentials near 0.2 V, to Co_3O_4 ; and at potentials between 0.25 and 0.35 V, to Co_2O_3 . Conway, *et al.*²⁴ and Göhr²⁵ found evidences for CoO and Co_3O_4 in the passive films on cobalt. Sato and his coworkers⁷ found from their ellipsometric data that the passive film formed at low potentials to be CoO. At higher anodic potentials, they concluded that the films are made of two layers, the inside one being CoO and the outside one Co_3O_4 or Co_2O_3 depending on the potential. The three-parameter ellipsometry data of the present work do not show an indication of duplex films in the potential range studied. The $dQ/d\tau$ slopes did not change during the growth of a passive film at each potential. This indicates that the films are of uniform compositions. In the present study, unlike in the work of Sato, *et al.*, potentials higher than 0.4 V *vs.* SCE were not applied in order to avoid roughening of the surface. It should be noticed that there is no abrupt change in any of the optical constants derived from the present transient data during the passivation stage. Therefore, the films seem to undergo a gradual change instead of a sudden phase-transition type

Table 1. Variation rate of coulombic charge expended for film growth, Q with film thickness, τ , compared to the calculated values for some known oxides of cobalt, and the optical constants of films grown at various potential ranges

Potential V <i>vs.</i> SCE	$dQ/d\tau$ $\text{mCcm}^{-2}/\text{nm}$	Calculated $dQ/d\tau$ for compounds of known densities	n_f	k_f
$-0.10-0.15$	1.67	1.66 for CoO (6.45 g cm^{-3})	2.02-2.05	0.40-0.43
0.20	1.96	1.94 for Co_3O_4 (6.054 g cm^{-3})	2.13	0.45
0.25-0.35	1.83	1.81 for Co_2O_3 (5.20 g cm^{-3})	2.15-2.16	0.46-0.47

of change. It also should be noted that, at any stage during the film formation, the imaginary part of the optical constant, k_p , does not have a near-zero value which might be associated with an electronically insulating property of the anodic film. Such was the case with the passive films on iron and nickel as reported previously.¹⁶⁻¹⁸ These transient behaviors, therefore, seem to be a general trend among passive films on metals such as iron, nickel, and cobalt.

Summary

By means of transient recordings of the three-parameter ellipsometry measurements, the thickness and the optical constants of passive film forming on cobalt under potentiostatic condition were determined as functions of time. The film-free reference surface of cobalt for the optical measurements was obtained by complete cathodic reduction of the surface film in the presence of EDTA. The growth of the passive film was mostly complete in 3-4 seconds from the onset of the passivating potential, and was followed by a slight decrease in the thickness in the time range of 4-40 s. The optical constants of the passive film showed gradual changes during the changes in the thickness. The thickness and the optical properties at the steady state of passivation depended on the potential of the electrode. From the coulometric and optical data, the composition of the passive films was deduced to be close to CoO at potentials lower than 0.15 V vs. SCE, to Co₂O₃ at higher potentials in the 0.25 to 0.35 V range, and to Co₃O₄ at intermediate potentials. It is concluded that the passive films undergo a gradual change during the passivation instead of a phase-transition type of change, since no abrupt change in the optical constants of the passive film was observed.

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References

1. C. A. Melendres and S. Xu, *J. Electrochem. Soc.*, **131**, 2239

- (1984).
2. G. W. Simmons, E. Kellerman, and H. Leidheiser Jr., *ibid.*, **123**, 1276 (1976).
3. J. Chon and W. Paik, *J. Korean Chem. Soc.*, **18**, 391 (1974).
4. T. Ohtsuka and N. Sato, *J. Jpn. Inst. Met.*, **39**, 60 (1975).
5. T. Ohtsuka, K. Kudo, and N. Sato, *ibid.*, **40**, 124 (1976).
6. N. Sato and T. Ohtsuka, *J. Electrochem. Soc.*, **125**, 1735 (1978).
7. N. Sato and T. Ohtsuka, *ibid.*, **128**, 2522 (1981).
8. W. Paik and J. O'M. Bockris, *Surface Sci.*, **28**, 61 (1971).
9. S. H. Kim, W. Paik, and J. O'M. Bockris, *ibid.*, **33**, 617 (1972).
10. S. Gottesfeld and B. Reichman, *ibid.*, **44**, 377 (1974).
11. J. Horkans, B. D. Cahan, and E. Yeager, *ibid.*, **46**, 1 (1974).
12. S. Gottesfeld, M. Babai, and B. Reichman, *ibid.*, **56**, 355 (1976).
13. W. Paik and Z. Szklarska-Smialowska, *ibid.*, **96**, 401 (1980).
14. W. Paik, in: "Electrochemistry", *International Review of Science, Physical Chemistry Series One, Vol. 6*, J. O'M. Bockris ed., Butterworth, 1973.
15. B. Park, W. Paik, and I. Yeo, *J. Korean Chem. Soc.*, **22**, 365 (1978).
16. D. Kim and W. Paik, *ibid.*, **26**, 369 (1982).
17. I. Yeo and W. Paik, *ibid.*, **28**, 271 (1984).
18. Y. Kang and W. Paik, *Surface Sci.*, **182**, 259 (1987).
19. Z. Szklarska-Smialowska, T. Zakroczymski, and C. J. Fan, *J. Electrochem. Soc.*, **132**, 2543 (1985).
20. T. Zakroczymski, Z. Szklarska-Smialowska, *ibid.*, **132**, 2548 (1985).
21. *American Institute of Physics Handbook*, 3rd ed., 1972.
22. R. J. Powell and W. E. Spicer, *J. Phys. Review B*, **2**, 2182 (1970).
23. J. G. Cook and G. C. Aers, *Surface Sci.*, **166**, 333 (1986).
24. K. J. Boyle, E. G. King, and K. C. Conway, *J. Am. Chem. Soc.*, **76**, 3835 (1954).
25. H. Göhr, *Electrochim. Acta*, **11**, 827 (1966).

The Analytical Solutions for Finite Clusters of Cubic Lattices

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Using the Hückel method, we obtain the analytical expressions for eigenvalues and eigenvectors of s.c., f.c.c. and b.c.c. clusters of rectangular parallelepiped shape, and of an arbitrary size. Our formulae converge to those derived from the Bloch sum, in the limit of infinite extension. DOS and LDOS reveal that the major contribution of the states near Fermi level originates from the surface atoms, also symmetry of DOS curves disappears by the introduction of 2nd nearest neighbor interactions, in all the cubic lattices. An accumulation of the negative charges on surface of cluster is observed.

Introduction

There are two major approaches in explaining the proper-

ties of solid. One is solid state physics in which a solid is regarded as a set of atoms or molecules of a large number, which is considered to have translational symmetry. The