CHARGE TRANSFER IN THE Ni/SiO_x/n-Si(111) SYSTEM

B VISWANATHAN [1], Katsumi TANAKA and I. TOYOSHIMA
The Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

Received 9 October 1984; in final form 6 November 1984

Binding energies of the core level (Ni $2p_{3/2}$) and LMM Auger peak have been measured for the system Ni/SiO_x/p- or n-Si(111) with different coverages of nickel. The Auger parameter was used to evaluate the relaxation shift from which the extent of chemical shift was deduced The binding energy shift has been shown to be a function of the thickness of oxide layer. The differences in the behaviour of the substrates formed from n- and p-type silicon show that charge transfer, though it can account for the observation on the substrate from n-type Si, is dependent on a number of factors like position and density of donor states and tunneling width.

1. Introduction

The elucidation of the nature and valence state of metal atoms dispersed on oxide supports has gained importance recently due to two experimental observations: (i) metals supported on TiO_2 and other reducible oxides show altered chemisorption capacities [1] and catalytic behaviour [2] as a result of reduction with hydrogen at higher temperatures; (ii) powdered semiconductors, especially TiO_2 and WO_3 containing controlled quantities of metallic elements like Pt, Pd and Cu, show great potential as photocatalysts, and their preparation by photoreduction techniques provides a novel method for controlled loading of metals on supports [3]. The former phenomenon, known as strong metal support interaction (SMSI), is variously explained in terms of concepts like poisoning by impurities [4], hydrogen retention [5], particle morphology [6], encapsulation of metal particles by the support [7], alloy formation [8] and charge transfer between the metal and the support [9]. Experimental evidence is available for each of these postulates, but has not established conclusively the cause of SMSI behaviour. The electronic structure studies of model systems for this behaviour by electron spectroscopic methods [9–13] have led to conflicting reports, some postulating charge transfer from the support to the metal, some providing evidence for charge transfer in the opposite direction or for no charge transfer. The reason for these conflicting reports is not clear at the moment, though one can consider that situations existing in thin film model systems with oxidized metallic substrates [13] may not be ideal for evaluating the initial state (chemical shift) effects as a result of metal dispersion since there is already a metal–metal oxide interface on one side. In this communication, the results of XPS and AES studies of a model system consisting of varying amounts of nickel deposited on oxidized single-crystal silicon thin films are presented. The choice of the substrate, namely n- and p-type silicon, is based on the possibility that the direction of charge transfer, if present, can be resolved.

[1] On leave from the Department of Chemistry, Indian Institute of Technology, Madras 600 036, India.

2. Experimental

The experiments were performed with a VG ESCA 3 photoelectron spectrometer under pressure typically of the order of $(6-8) \times 10^{-11}$ Torr. Photoelectron spectra were recorded using a VG dual anode X-ray source operating the Mg anode ($h\nu = 1253.6$ eV). Silicon(111) single crystals (approximate size of 1 cm^2) of n- and p-type obtained by doping with either P or

0 009-2614/85/$ 03.30 © Elsevier Science Publishers B.V (North-Holland Physics Publishing Division)

B to the extent of 1×10^{16} atoms/cm^3 Si (typical specific resistivity of p-type crystal is about 16 Ω cm and that of n-type crystal is about 2000 Ω cm) were mounted on the sample holder by means of tantalum wire. Surface impurities on the substrate (namely carbon and oxygen) were removed by prolonged (usually overnight) Ar ion bombardment with intermittent heating to 873 K. The surface layers were oxidized by exposing to 10^{-7} Torr oxygen for 5 or 20 min at 800 K These oxidation conditions led to an oxide film which gave an XP spectrum with peaks at 99.3 eV for Si^0 and a broad peak at 102.1 eV due to surface oxide both referred to carbon at 284.6 eV. This surface oxide can be considered as a reduced form of SiO_2 as the binding energy of Si in thin film of Si_2O_3 has a value of 102 eV and in SiO_2 at 102.65 eV [14]. The uniformity of the oxide layer was confirmed by analysis of different regions of the same sample or of different samples prepared under identical conditions. The absence of a charging effect was deduced by the constancy of the Si XPS peak as a function of X-ray exposure time or with small variations in X-ray flux. Controlled amounts of nickel were deposited on this substrate using a doser, consisting of a resistively heated W filament wrapped with a JMC high-purity nickel wire of 0.5 mm diameter The substrate was placed approximately 4 cm from the filament in a position such that macroscopically uniform coverage of the metal deposition could be obtained. A typical dose rate of 0.2 ML min^{-1} as determined from the time dependence of Auger and XPS signals of nickel and silicon could be obtained by adjusting the current passing through the filament. The surface carbon level was maintained at the lowest level at all stages of these experiments with considerable effort.

Since an ideal layer-by-layer growth model has been shown to be applicable for metal deposition on oxide substrates in the low-coverage region [13], this procedure of calibration using a value of 14.5 Å [15, 16] for the electron inelastic mean free path for nickel (λ_{848}), is adopted for estimating the extent of metal coverage at each stage of deposition. The plot of the intensity ratio of the XPS signals of Ni $2p_{3/2}$ (854 eV) and Si 2p (99.3 eV) also showed gradient changes at these times supporting the use of this method of calibration for determining the coverage values. In this sense, the coverages reported can be considered to be indicative and not absolute.

3. Results

3.1. *Characterization of oxide formed on silicon(111)*

Lang et al. [17] studied the oxidation of Si(111) at 773 K and concluded from the fine structure analysis of the Auger silicon $L_{2,3}VV$ signal at 91.0 eV that attenuation values (h_{Si}/h^0_{Si}, where h_{Si} and h^0_{Si} are the peak-to-peak heights of silicon signal after and before oxidation, respectively) become greater than 0.75 when only SiO_x ($x < 2$) species are formed, smaller than 0.15 when only SiO_2 is formed, while at attenuation values in between these limits both SiO_2 and SiO_x species are formed. In the present case, a typical value of the attenuation parameter for thin oxide (formed by oxidation for 5 min) is approximately 0.5 showing that in the oxide overlayer both SiO_2 and SiO_x species coexist The presence of SiO_2 is also deduced from the Auger lines around 65 eV [18]. The attenuation values can be converted to thickness using the value of the mean free path λ of the Auger electrons which was taken as 6.5 Å, a mean value of λ = 5.5 Å reported for a room-temperature oxidized layer [19] and λ = 7.5 Å for a thick silicon oxide [20] using the relation $h_{Si} = h^0_{Si} \exp(-d/0.74\lambda)$. On the basis of this estimate, the thin oxide layer (obtained by oxidation for 5 min) can be 3–4 Å thick and the thick oxide layer obtained by oxidation for 20 min is of the order 8–10 Å thick. These estimates agree with those reported by Lang et al. [17]. The thickness of the oxide layers thus estimated is also in agreement with the evaluation based on the sputtering rate. Assuming unit sputtering yield (S), the rate of sputtering is calculated using the relation [16] $Z = (M/\rho N_A e) S J_p$, where M is the mass number, ρ is the density (kg/m^3), N_A is Avogadro's number, e the electronic charge, and J_p is the primary ion current density (A/m^2). For a typical value of 10^{-1} A/m^2, the estimated sputtering rate is 10^{-2} nm/s and since the thick oxide layer could be sputtered in about 2 min, one obtains a thickness value of 10–12 Å which is in agreement with the value deduced from AES measurements Similar estimates were made from XPS intensity data using a mean free path λ_{Si} (1178 eV) of 39 Å [21].

3.2. *Deposition of nickel on SiO_x/Si(111) system*

Typical valence band spectra for different cover-

ages of nickel on thick silicon oxide (10–12 Å) on n-type Si(111) are shown in fig. 1. The binding energy scale is calibrated by referencing to carbon 1s (284.6 eV). It is seen that emissions from the 13.8 and 9.3 eV peak are both attenuated with increasing coverage, though to a smaller extent for the 9.3 eV peak. The energy difference between these peaks and also their positions remain constant with respect to nickel coverage. Deposition of nickel generates emission levels in the band gap and it increases with nickel coverage and moves towards the lower binding energy side. These features were also observed with substrates containing thin oxide layer (4–5 Å) on n- or p-Si(111) as well as thick oxide layer on p-Si(111). However, the position of the peaks (at 9.3 and 13.8 eV) in the valence band region remained unchanged with respect to nickel coverage for these systems also.

Figs. 2 and 3 show the positions of Ni $2p_{3/2}$ peak and Ni $L_3M_{2,3}M_{2,3}$ Auger peak for n-Si(111) substrate with thick oxide (10–12 Å) layer as a function of nickel coverage θ, respectively. The Ni $2p_{3/2}$ peak shifts to lower binding energy by 0.4 eV as θ increases from 0.15 to 10. Correspondingly the Auger peak shifts by 3 eV to higher kinetic energy. At low coverages of nickel the separation between Ni $2p_{3/2}$ and Ni $2p_{1/2}$ is slightly less than 17.4 eV, though at higher coverages this value of separation is attained. Similar results were obtained with thin oxide (4–5 Å) on

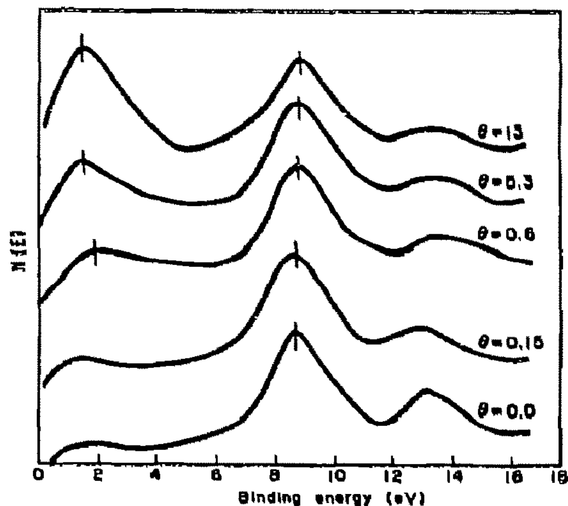

Fig. 1. Valence band spectra of the thick oxide substrate (10–12 A) on n-Si(111) as a function of nickel coverage θ.

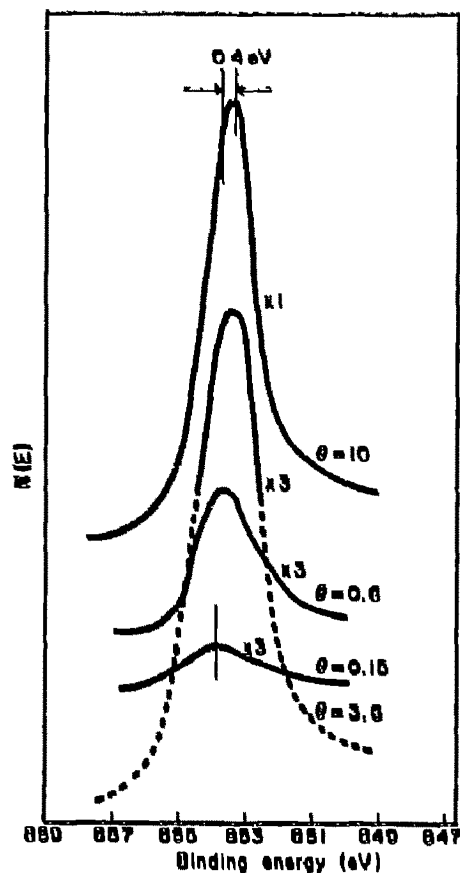

Fig. 2. The Ni $2p_{3/2}$ peak for Ni deposited on thick oxide substrate (10–12 Å) on n-Si(111) as a function of nickel coverage θ.

n-Si(111) with a slightly higher binding energy shift fc the Ni $2p_{3/2}$ level. However, no such shift could be observed for Ni $2p_{3/2}$ peak when deposited on oxide layer formed on p-Si(111). The results of these studies are summarized in table 1.

Using similar data for Pt on $SrTiO_3$ and Ni on TiO single crystal, Chung and co-workers [9] have extracted the extents of relaxation (ΔR) and chemical shifts (ΔE) using the relations

$$\Delta(\mathrm{BE}) = \Delta E - \Delta R - \Delta E_{\mathrm{bonding}}\,, \quad (1)$$

$$\Delta(\mathrm{KE}) = -\Delta E + 3\Delta R + \Delta E_{\mathrm{bonding}}\,, \quad (2)$$

where $\Delta E_{\mathrm{bonding}}$ is the change in the measured energy due to band bonding. The adequacy of these expressions for accurately determining chemical shifts (the

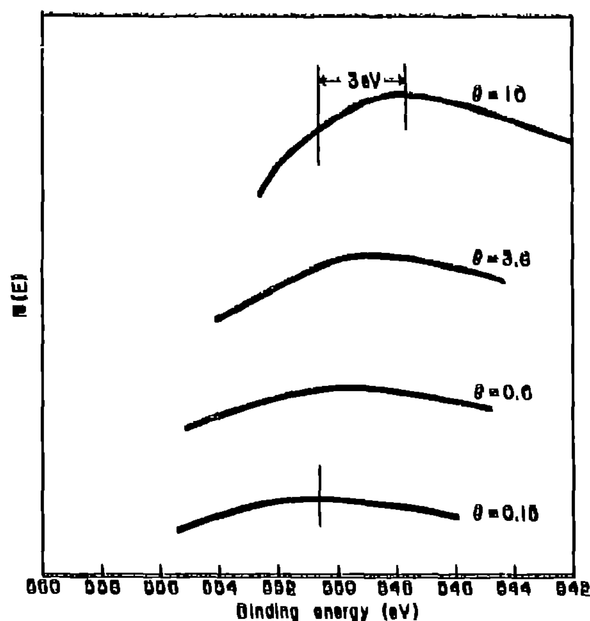

Fig. 3. The Ni $L_3M_{2,3}M_{2,3}$ peak on thick oxide substrate (10–12 Å) on n-Si(111) as a function of nickel coverage θ.

initial state effect) has been debated [10,13,22] and it is considered that corrections up to 3 eV are warranted in some situations. This is probably true as seen from the data given in table 1. The system with higher binding energy shift (thin oxide on n-type silicon) shows lower chemical shift if these two expressions are used to compute this parameter.

4. Discussion

The postulate that the cause of SMSI behaviour is due to charge transfer from the support to the metal is a controversial one. Based on the results of XPS and AES studies of Pt on single crystal $SrTiO_3$ and nickel on single crystal TiO_2, Chung and co-workers [9] concluded in favour of this postulate. Huizinga et al. [10] observed that there is no binding energy shift as a function of metal deposition or reduction in the case of Rh/TiO_2 and $Rh/\gamma\text{-}Al_2O_3$. Similarly, there is no difference in the behaviour of the oxidized and reduced forms of Pt on TiO_2 powder system. Belton et al. on the basis of the result that suppressed chemisorption could be observed even after extended (2–3) monolayers of Pt on TiO_2, concluded that charge transfer could not cause SMSI behaviour, since the charge-screening length in metallic systems cannot be greater than one lattice spacing [13]. As pointed out by Huizinga et al. [10] there may be difficulties in the interpretation of Auger parameters especially with respect to extent of charge transfer as deduced by Chung and co-workers [9]. The results presented in table 1 support this conclusion especially with respect to the use of eqs. (1) and (2) for the estimation of initial state effects (chemical shift). However, the charge transfer model can account for the two observations recorded in the present study, namely, (i) the shift in the binding energy of Ni $2p_{3/2}$ level is larger for the substrate with thin oxide layer on n-type silicon as compared with the substrate containing a thick oxide layer; and (ii) no shift is observed on the substrate formed from p-type silicon, irrespective of the thickness of oxide layer formed.

Table 1
The nickel $2p_{3/2}$ binding energy and $L_3M_{2,3}M_{2,3}$ Auger shift as a result of nickel deposition on oxide substrates formed on silicon single crystals

Surface	ΔBE (eV)	ΔKE (eV)	ΔE (eV)	ΔR (eV)
thick oxide (10–12 Å) on n-Si(111)	0.4	−3.0	−0.9	−1.3
thin oxide (4–5 Å) on n-Si(111)	1.0	−4.0	−0.5	−1.5
thin oxide (4–5 Å) on p-Si(111)	0.1 [a]	−1.0	–	–

[a] Since this value is within our experimental error, it is not considered. ΔBE and ΔKE values were taken between θ = 10 and the lowest θ value we could measure (that is ≈0.15). θ is the nickel coverage.

The availability of a high density of donor states in n-type silicon above the lowest unoccupied levels of nickel atoms or even clusters favours the charge transfer from the semiconductor to the metal. However, the acceptor states in p-type silicon can still be higher than the highest occupied levels of nickel atoms or clusters. In this model, charge transfer by tunnelling from silicon semiconductor has to be invoked since the substrates obtained from n- and p-type silicon behaved differently. However, a semiconducting oxide with high density of donor states can function in the same mode and this is probably the situation existing in the highly reduced forms of oxide supports used for observing the SMSI behaviour. Particle size effects may sometimes complicate the situation thus precluding the observation of this effect by XPS analysis. However, one would expect the same morphology for the nickel deposited on substrates obtained from both n- and p-type silicon.

In conclusion, this study showed that on well characterized SiO_x/n- or p-Si substrates, deposition of nickel in a nearly atomic state at submonolayer levels resulted in the shift of the binding energy of the Ni $2p_{3/2}$ level only when the substrate was formed from n-type silicon single crystal. This means that charge transfer from the support to the metal is perceptible only when the substrate contains a high density of donor states at appropriate energy values.

Acknowledgement

We acknowledge with thanks the fellowship to one of us (BV) from the Japan Society for the Promotion of Science (JSPS). We also thank Dr. Yatsurughi, Komatsu Electronics, Japan, for kindly supplying n- and p-type silicon single crystals. This work was partly supported by a Grant-in-Aid for Scientific Research (No 5670062) from the Ministry of Education of Japan (IT).

References

[1] S.J. Tauster, S.C. Fung and R.L. Garten, J. Am. Chem. Soc. 100 (1978) 170;
S.J. Tauster and S.C. Fung, J. Catal. 55 (1978) 29.

[2] E.I. Ko, J.M. Hupp and N.J. Wagner, J. Catal. 86 (1984) 315;
O. Okada, M. Ipponmatsu, M. Kawai, K. Aika and T. Onishi, Chem. Letters (1984) 1041

[3] R.I. Bickley, Specialist Periodical Reports. Catalysis, Vol. 5 (Chem. Soc., London, 1982) p. 308.

[4] J. Wang, J.A. Lerche and G.L. Haller, J. Catal. 88 (1984) 18.

[5] J.C. Conesa, P. Malet, G. Munuera, J. Sanz and J. Soria, J. Phys. Chem. 88 (1984) 2986.

[6] R.T.K. Baker, E.B Prestridge and R.L. Garten, J. Catal 56 (1979) 390; 59 (1979) 293.

[7] A.J. Simoens, R.T.K. Baker, D.J. Dwyer, C.R.F Lund and R.J. Madon, J. Catal. 86 (1984) 359;
G.B. Raupp and J.A. Dumesic, J. Phys. Chem. 88 (1984) 660;
D.N. Belton, Y.M. Sun and J.M. White, J. Am. Chem Soc. 106 (1984) 3059;
M.A. Vannice and C. Sudhakar, J. Phys. Chem. 88 (1984) 2429;
H.R. Sadeghi and V.E. Henrich, J. Catal. 87 (1984) 279.

[8] R.Y. Tang, R.A Wu and L.W. Lin, Appl. Catal. 10 (1984) 163.

[9] M.K. Bahl, S.C. Tsai an Y.W. Chung, Phys. Rev B21 (1980) 1344;
C.C. Kao, S.C Tsai and Y.W. Chung, J Catal. 73 (1982) 136;
C.C. Kao, S.C. Tsai, M.K. Bahl and Y.W. Chung, Surface Sci 95 (1980) 1.

[10] T. Huizinga, H.F.J. Vant Blik, J.C. Vis and R. Prins, Surface Sci. 135 (1983) 580.

[11] B.A. Sexton, A.E. Hughes and K. Foger, J. Catal. 77 (1982) 85;
S H. Chien, B.N Shelimov, D.E. Resasco, E.H. Lee and G.L. Haller, J. Catal. 77 (1982) 301;
M. Koudelka, A. Monnier, J. Sanchez and J Augustynski, J. Mol. Catal. 25 (1984) 295.

[12] B.H. Chen and J.M. White, J. Phys Chem. 86 (1982) 3534;
T.H. Fleisch, R.F. Hicks and A T. Bell, J. Catal. 87 (1984) 398.

[13] D.N. Belton, Y.M Sun and J.M. White, J. Phys Chem 88 (1984) 1690

[14] T.L. Barr, Appl. Surface Sci 15 (1983) 1.

[15] C.C. Chang, Surface Sci. 48 (1975) 9.

[16] D. Briggs and M.P. Seah, Practical surface analysis (Wiley, New York, 1983).

[17] B. Lang, P. Scholler and B. Carriere, Surface Sci. 99 (1980) 103.

[18] H.H. Madden, J. Vacuum Sci. Technol. 18 (1981) 677;
R. Weissmann, R. Koschatzky, W. Schnellhammer and K. Muller, Appl. Phys. 14 (1977) 284.

[19] C.C. Chang and D.M. Boulin, Surface Sci. 69 (1977) 385.

[20] C.M. Garner, I. Lindau, C.Y. Su, P. Pianetta and W.E. Spicer, Phys. Rev. B19 (1979) 3944.

[21] M. Klasson, A. Berndtsson, J. Hedman, P. Nilsson, R Nyholm and C. Nordling, J. Electron Spectry. 3 (1974) 427.

[22] T.D. Thomas, J. Electron Spectry. 20 (1980) 117.