

## CO Adsorption Suppression due to Charge Transfer in the Ni-SiO<sub>x</sub>-n-Si(111) System at Low Ni Coverage

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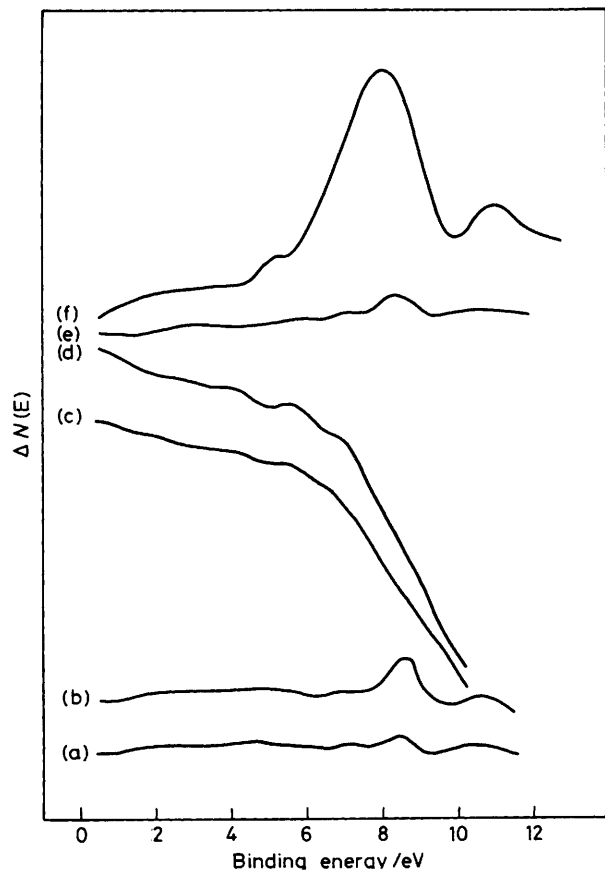
No CO adsorption was observed in the He I u.v. photoelectron spectra at low Ni coverage on SiO<sub>x</sub>-n-Si(111) where charge transfer has been concluded to occur, whereas normal CO adsorption was observed at low Ni coverage on SiO<sub>x</sub>-p-Si(111) or at high Ni coverage on SiO<sub>x</sub>-n-Si(111); these results show that charge transfer occurring in a narrow region at low Ni coverage is responsible for the suppression of CO adsorption.

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Interactions between metals and semiconductors have attracted much interest; electronic interactions have been reported for Pt-SrTiO<sub>3</sub>(100)<sup>1</sup> and Ni-TiO<sub>2</sub>(100).<sup>2</sup> We recently reported that charge transfer takes place in the Ni-SiO<sub>x</sub>-n-Si(111) system at low Ni coverage irrespective of the thickness (4—5

or 10—12 Å) of the oxide layer.<sup>3</sup> We now show that charge transfer plays an important chemical role in the inhibition of molecular adsorption capability for CO.

The experiments were performed with a VG ESCA 3 photoelectron spectrometer under a pressure typically of 6—8



**Figure 1.** The difference He I u.v. photoelectron spectra following CO exposure to Ni-SiO<sub>x</sub>(4–5 Å)-n- or -p-Si(111) at room temperature. (a) 1L and (b) 18 L of CO on Ni-SiO<sub>x</sub>-p-Si(111) for  $\theta_{\text{Ni}} = 0.3\text{--}0.4$ ; (c) 1L and (d) 18 L of CO on Ni-SiO<sub>x</sub>-n-Si(111) for  $\theta_{\text{Ni}} = 0.3\text{--}0.4$ ; (e) 1L and (f) 18 L of CO on Ni-SiO<sub>x</sub>-n-Si(111) for  $\theta_{\text{Ni}} = 20$ .

$\times 10^{-11}$  Torr. Silicon(111) single crystals of n- and p-type, obtained by doping with either P or B to the extent of  $1 \times 10^{16}$  atom/cm<sup>3</sup>Si (typical specific resistivity of p-Si is  $\sim 16 \Omega \text{ cm}$  and that of n-type crystal is  $\sim 2000 \Omega \text{ cm}$ ), were used. The surface impurities on the substrate (carbon and oxygen) were removed by prolonged Ar ion bombardment with intermittent heating to 873 K. The surface layer was oxidized by exposure

to  $10^{-7}$  Torr of O<sub>2</sub> for 5 min at 800 K. Surface analysis of the oxidized substrate showed that the surface oxide layer can be considered as a reduced form of SiO<sub>2</sub>, with a thickness of 4–5 Å.<sup>3</sup> Controlled amounts of Ni were deposited on SiO<sub>x</sub>-n- or -p-Si(111) at room temperature with a typical dose rate of 0.2 ML min<sup>-1</sup> as determined from the time dependence of Auger and X-ray photoelectron signals of Ni and Si. The surface carbon could be maintained at the lowest level at all stages of these experiments.

Figure 1 shows the results of CO exposure experiments with the Ni-SiO<sub>x</sub>-Si(111) system at room temperature. Difference spectra were obtained to eliminate an intense peak at about 5 eV due to oxygen from the surface silicon oxide. If CO is adsorbed molecularly, two peaks are seen at  $\sim 8$  and 11 eV assigned as emission from the  $5\sigma + 1\pi$  and  $4\sigma$  levels, while dissociatively adsorbed CO is evident from a peak at  $\sim 5$  eV due to C 2p and/or O 2p. Two peaks were observed at 8.6 and 10.6 eV when 1 L of CO was exposed to Ni-SiO<sub>x</sub>-p-Si(111) with low Ni coverage ( $\theta = 0.3\text{--}0.4$ ) and their intensities increased as the CO dose increased [Figure 1(a,b)]. The reason for the small peak-to-peak value (2 eV) is not yet known. However, no CO adsorption was observed with the same amount of Ni deposited on the SiO<sub>x</sub>-n-Si(111) system [Figure 1(c,d)]. Suppression of CO adsorption for the Ni-SiO<sub>x</sub>-n-Si(111) system occurred for low Ni coverages since CO adsorption was obvious at high coverages ( $\theta = 20$ ) [Figure 1(e,f)] where the Ni state is almost identical to that of the bulk metal.

In our system, charge transfer occurs from the donor level of n-Si to Ni across the thin silicon oxide layer probably by electron tunnelling. However, it does not occur from Ni to the acceptor level of p-Si.<sup>3</sup> Electron-charged Ni shows no CO adsorption ability and this effect is applicable only when a small amount of Ni is present on the surface.

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