PREPARATION AND REACTIVITY OF Cu(100)-Ni SURFACES

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Received 15 December 1980; accepted for publication 9 February 1981

A novel way of preparing Cu(100)-Ni single crystal surfaces is described. Reproducible quantities of nickel are deposited on a clean Cu(100) surface via reaction of nickel carbonyl. The chemical properties of this surface as monitored by AES and ellipsometry are investigated with respect to oxygen uptake and reduction (CO) reactions. At low Ni concentration the nickel atoms appeared to be below the first monolayer of copper atoms and are incapable of binding CO at room temperature and pressures up to 10^{-3} Torr CO. At exposures up to 2500 L and at 320° C, the surface takes up more oxygen than a clean Cu(100) surface but less than clean Ni(100).

1. Introduction

Cu-Ni alloys have been the topic of many investigations [1-17]. Especially the surface composition [1-4] and its relation with respect to adsorption [5-17] have been extensively studied. It is generally accepted that the surfaces of annealed Cu-Ni single crystals, as well as the surfaces of Cu-Ni films prepared by evaporation, are enriched in copper.

The adsorption of CO [5-12] can be described as a site effect [6,9,11,12]. Thermal desorption spectra show CO desorption from a Ni site, a Cu site and two mixed Cu-Ni sites [6] for the (110) surface. Measurements of the change of the work function during CO desorption support this model and show that one of the mixed sites can be described as "Cu-like" and the other as "Ni-like" [11,12].

The oxidation of Cu-Ni alloys has been less extensively studied [13-17]. Using AES/LEED Ertl and Küppers found that oxygen adsorption on Cu-Ni(110) depends on the individual properties of Cu and Ni towards oxidation [14]. Oxygen chemisorption does not saturate as on Cu(110), but continues while nickel migrates to the surface. This segregation is explained by the minimum surface energy model and was also mentioned by Helms and Yu [13], these authors observed, however, nickel segregation only at elevated temperatures.

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The interaction of CO with preadsorbed oxygen on Cu–Ni single crystals has not been studied extensively, although the reaction of CO with oxygen on copper and nickel differs very much; surfaces with adsorbed oxygen can be almost totally reduced with CO [18–20] in contrast to nickel surfaces [21].

In the present investigation we report on the properties of Cu–Ni surfaces prepared by decomposing Ni(CO)₄ on a hot Cu(100) single crystal. In this way the amount of nickel in the surface layer can be controlled reproducibly, since after sputter-cleaning of the crystal a clean Cu(100) surface can again be obtained.

2. Experimental

The experiments were carried out in a stainless-steel UHV system pumped with a turbo-molecular pump, an ion-getter pump and a titanium-sublimation pump. After bake-out at 200°C for 60 h a pressure of 10^{-10} Torr (1 Torr = 133.33 Pa) was reached. The system was equipped with facilities for ellipsometry, AES and LEED. A more detailed description is found in ref. [22].

The Auger spectra were recorded with a four-grid retarding field analyzer. The current of the primary beam was 30 μ A, its energy 2500 eV and the angle of incidence $7 \pm 1^{\circ}$ with the surface. The modulation voltage on the grids was $1 V_{p-p}$ for the lower energy part (95–115 eV) of the spectra and $10 V_{p-p}$ for the higher part (115–1000 eV). The ellipsometric arrangement and procedure was as described in ref. [23]. The changes in the ellipsometric angles $\delta \Delta (\equiv \overline{\Delta} - \Delta)$ and $\delta \psi (\equiv \overline{\psi} - \psi)$ ($\overline{\Delta}, \overline{\psi}$: clean surface) were determined with two-zone measurements (interrupted exposures) or by off-null irradiance measurements (continuous exposures). The wavelength was 632.8 nm and the angle of incidence $69 \pm 1^{\circ}$. The crystal was disk-shaped (diameter 6 mm), spark-cut from a 5N copper rod (Material Research Corporation) to within 2° of the (100) orientation. It was electro-lap polished and mounted in a stainless-steel crystal holder. The surface was cleaned by applying cycles of sputtering (600 eV, $5 \,\mu A \, \text{cm}^{-2}$, $10^{-4} \, \text{Torr Ar}$) and annealing (450°C). Auger spectra showed that the amount of any contaminant on the surface was less than about 3% of a monolayer.

The gases used, i.e. argon (99.999%), oxygen (99.995%) and carbon monoxide (99.997%) were purchased from L'Air Liquide. During all exposures the gas was continuously renewed by pumping with the turbo-molecular pump. For safety reasons the nickel carbonyl was prepared in a small stainless-steel cylinder (20 cm³), directly connected to the gas-handling manifold. Ni(CO)₄ was synthesized from Ni pellets (height and diameter 5 mm, Fluka 99.9999%), previously reduced for 48 h at 300°C in a flow of 10% hydrogen in Ar. The initial CO pressure was 2 bar. We checked our experiments with pure Ni(CO)₄ (Matheson 99.9%) which gave the same results. The exhaust of the pump was connected to a furnace, kept permanently above 300°C, in order to destroy the extremely poisonous Ni(CO)₄. The equilibrium of the reaction Ni(s) + 4 CO(g) \Rightarrow Ni(CO)₄(g) depends strongly on the



Fig. 1. Calculated partial nickel carbonyl pressures (bar) as a function of the total pressure for the reaction $Ni(s) + 4 CO \Rightarrow Ni(CO)_4$ at room temperature.

total pressure $(P_t = P_{CO} + P_{Ni(CO)_4})$. Fig. 1 shows the Ni(CO)₄ pressure as a function of the total pressure at room temperature, where $k_p = 4.2 \times 10^6 \text{ bar}^{-3}$ [24]. From this figure it is clear that Ni(CO)₄ should decompose at low pressures (~1 Torr in the gas-handling manifold), but this reaction is slow at room temperature. The composition of the Ni(CO)₄-CO gas mixture is, however, unknown. Therefore the exposures mentioned below do not correspond to the actual Ni(CO)₄ pressure, but are the products of total pressure and time.

3. Results

3.1. Reaction of Ni(CO)₄ with Cu(100)

At exposures below 6×10^4 L the reaction of the Ni(CO)₄--CO mixture with the clean annealed Cu(100) surface is followed by ellipsometry, AES and LEED, while at larger exposures AES and LEED served as surface monitors. After exposures at temperatures below 150°C Auger spectra showed besides Cu and Ni, C and O. At higher temperatures (200-400°C) only Cu and Ni were detected. With AES we measured the peak to peak heights of Ni(M₁M_{4,5}M_{4,5}) 101 eV, denoted by h₁₀₁,



Fig. 2. Low-exposure region of the deposition of Ni from Ni(CO)₄ on Cu(100) at 320° C. Encircled crosses, values of the Ni fraction calculated from the high-energy Auger peaks. The exposure scale is relative, as the actual nickel carbonyl pressure is unknown and may actually vary between the different measured points. Ellipsometric data are taken from two-zone measurements.

Ni($L_3M_{4,5}M_{4,5}$) and 848 eV and Cu($L_3M_{2,3}M_{4,5}$) 848 eV, h_{848} , Cu($M_1M_{4,5}M_{4,5}$) 104 eV, h_{104} , and Cu($L_3M_{4,5}M_{4,5}$) 920 eV, h_{920} . For a clean Cu(100) crystal the ratio h_{848}/h_{920} was measured to be 0.4.

In fig. 2 the changes in Δ and ψ , $\delta\Delta$ and $\delta\psi$, are shown together with the h_{848}/h_{920} and $h_{101}/(h_{101} + h_{104})$ Auger signals as a function of the exposure at 320°C. It can be seen that the h_{848}/h_{920} ratio changes immediately. This is due to an increase of the 848 eV Cu + Ni peak and a decrease of the 920 eV Cu peak. The 101 eV peak is not observed until higher exposures are reached. Deposition of Ni is accompanied by a decrease in ψ ($\delta\psi > 0$), the slope of $\delta\psi$ versus the exposure decreases with increasing exposure. The value of $\delta\Delta$ is negative at low exposures and becomes positive at higher exposures. We also monitored $\delta\psi$ continuously by off-null irradiance measurements. These data (not shown) are slightly different; at constant pressure $\delta\psi$ versus the exposure is a straight line while the rate of change of $\delta\psi$ appeared to be proportional to $P_{total}^{4/3}$. The difference between two-zone measurements and off-null measurements is probably due to a change in composition of the gas mixture in the gas-handling manifold which can be neglected for off-null measurements, which take 4-5 h.



Fig. 3. High-exposure region of the deposition of Ni from Ni(CO)₄ on Cu(100) at 320° : (\circ) nickel fractions calculated from the high-energy Auger peaks. Beyond expositions of about 6×10^4 L carbon was also observed in the AES spectra.

Fig. 3 shows the h_{848}/h_{920} and $h_{101}/(h_{101} + h_{104})$ ratios at higher exposures at 320°C. After 6×10^4 L, C also appears in the Auger spectra.

During all experiments the LEED pattern remained the usual (1×1) pattern of the clean Cu(100) surface. Only when carbon appeared in the Auger spectra we found an increase in background intensity but no change in the (1×1) pattern.

3.2. Interaction of CO with Cu(100)-Ni

Exposures of CO were carried out at room temperature and at pressures up to 10^{-3} Torr. We measured neither an irreversible (AES) nor a reversible (ellipsometry) adsorption of CO on Cu(100) which was covered with Ni up to $\delta \psi = 3^{\circ}$.

3.3. Interaction of O_2 with Cu(100)–Ni and reaction of CO with preadsorbed oxygen

Oxygen was exposed to a clean Cu(100)—Ni at a crystal temperature of 320°C and pressures up to 5×10^{-6} Torr. For this reaction we chose a Ni coverage corresponding with $\delta \psi = 0.7^{\circ}$ with respect to a clean Cu(100) because up to this coverage Auger spectra show no Ni 101 eV peak while the h_{848}/h_{920} ratio clearly differs from 0.4. The oxygen uptake and consecutive reduction of the surface with CO was monitored by means of off-null measurements. Fig. 4 shows $\delta\Delta$ versus the oxygen exposure to Cu(100)—Ni. The rate of change of $\delta\Delta$ decreases with increasing

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Fig. 4. Interaction of O₂ with Cu(100)–Ni at 320°C as observed with ellipsometry. The dotted lines give the experimental results for pure Cu(100) [20] and Ni(100) [25].

oxygen coverage but there is no sign of any saturation. For comparison, the curves for oxygen adsorption on Cu(100) [20] and Ni(100) [25] are also depicted in fig. 4.



Fig. 5. Reduction of a preoxidized Cu(100)–Ni surface by CO monitored with ellipsometry. The dotted line gives the result for pure Cu(100) [20]; $t = 320^{\circ}$ C.

Table 1

 $\delta\Delta$, with respect to clean Cu(100)–Ni, and the absolute Auger peak to peak heights for O 510 eV, Cu + Ni 848 eV and Cu 920 eV; the relative decrease in the metal signals upon oxygen adsorption is of similar magnitude as for the pure metals

	δΔ (deg)	h_{848} (Cu + Ni)	h920 (Cu)	h_{510} (O)
"Ol"			102	10
Clean	0	03	103	10
Ox. ads. 1	1.70	47	96	79
Red. 1	1.70 - 1.34 = 0.36	56	98	27
Ox. ads. 2	0.36 + 1.46 = 1.82	47	99	84
Red. 2	1.82 - 0.73 = 0.99	53	97	25
Ox. ads. 3	0.99 + 1.10 = 2.09	44	95	81
Red. 3	2.09 - 0.46 = 1.63	50	101	36

In fig. 5 the reduction at 320°C of a Cu(100)—Ni surface on which oxygen was deposited up to $\delta \Delta = 1.6^{\circ}$ is represented as $\delta \Delta$ versus the CO exposure. The rate of change of $\delta \Delta$ continuously decreased with decreasing oxygen coverage. After the first reduction reaction, when no more change in $\delta \Delta$ could be detected, an amount of oxygen corresponding to $\delta \Delta = 0.3^{\circ}$ and h_0/h_{920} ratio of 0.25 still remained on the surface. This quantity is much larger than the amount of oxygen still left after reaction of CO with oxygen on pure Cu(100), for comparison this reaction is also depicted in fig. 5.

In table 1 data for three consecutive oxygen adsorption and reduction cycles are given. The first column gives the change in $\delta\Delta$ after reaction with O₂ or reduction with respect to the clean Cu(100)—Ni value; also included are the values relative to the situation at the start of each cycle. The remaining columns give the absolute values of the h_{848} , h_{920} and oxygen 510 eV Auger peaks. Some oxygen was present at the beginning of the experiment. It will be noted that subsequent reductions leave progressively more oxygen at the surface which could not be removed by CO. Whereas the Cu 920 eV peak remains almost constant, the Cu—Ni 848 eV peak oscillates in intensity after reaction with oxygen or carbon monoxide.

4. Discussion

The first point we wish to discuss is the composition of the Cu-Ni surface prepared by the decomposition of Ni(CO)₄. Above 150°C only Ni is deposited onto a clean annealed Cu(100) single crystal; the carbonyl completely dissociates and CO desorbs. From fig. 2 it can be concluded that the nickel atoms first deposited are taken up below the surface layer of copper atoms, since the low-energy Ni Auger peak (101 eV) appears only at higher exposures, whereas the high-energy Ni peak (848 eV) shows up immediately. With Auger spectra measured using equal experimental conditions the ratio of the Cu 920 eV peak to the Ni 720 eV peak is 2.6 [26]. Together with $(h_{720}/h_{848})_{Ni} = 0.4$ [21] and $(h_{848}/h_{920})_{Cu} = 0.4$, a rough estimate of the fraction of Ni in the first 6–8 atomic layers can be made, when it is assumed that the escape-depths with Cu and Ni are equal at 720–920 eV. This amount of nickel is also given in figs. 2 and 3.

After exposures larger than 6×10^4 L, the surface layer contains almost exclusively Ni. Then carbon is deposited during the further decomposition of Ni(CO)₄. The gas mixture to which the surface is exposed consists of both Ni(CO)₄ and CO. The carbon deposition therefore maybe due to CO disproportionation to C_{ads} and CO₂. At temperatures below 150°C, besides Ni also C and O are deposited onto the copper surface, according to the Auger spectra. This may be explained by an incomplete dissociation of Ni(CO)₄ resulting in the adsorption of Ni(CO)_x ($x \le 4$) species. Another possibility is that the temperature of the crystal is too low to enable Ni atoms to penetrate below the first layer of Cu atoms; Ni atoms remaining at the surface are capable of binding CO.

It is interesting that CO molecules bonded to Ni atoms present in the Cu–Ni surface are much less liable to be dissociated by incident electrons than CO adsorbed on pure Ni. With a pure Ni surface, incident electrons rapidly dissociate adsorbed CO into carbon atoms taken up into the surface and desorbing oxygen, presumably as O⁺ ions. This may point to the fact that at least about three Ni surface atoms are required to bind sufficiently strongly a carbon atom set free by the above dissociation [27]. The number of triplets of Ni atoms at the Cu–Ni surface is too small to bind the carbon of all the adsorbed CO molecules. As a result a fraction of the adsorbed CO does not dissociate, which causes the oxygen Auger signal to remain stable during the electron bombardement required to excite Auger spectra.

At room temperature Cu(100) surfaces onto which nickel has been deposited above about 150°C are not able to adsorb CO, neither reversibly (ellipsometry) nor irreversibly (AES). Even with Ni contents giving rise to $\delta\psi$ values of 3°, which correspond to $h_{101}/(h_{101} + h_{104}) \sim 0.25$, no adsorption of CO is observed. This agrees with the Ni atoms being taken up below the surface. At more elevated Ni contents, nickel atoms must be present at the surface, as a Ni 101 eV Auger peak is observed. The surface nevertheless does not adsorb CO, possibly due to the absence of a marked fraction of nickel doublets in the surface, that can bind CO bridge-like [28]. Alternatively the reactivity of nickel surface atoms surrounded by copper atoms may be different from the surface atoms of pure nickel, if also linearly bonded CO is assumed to exist. A third reason for this observation might be that the actual Ni concentration at the surface is grossly overestimated by the AES results, due to the existence of concentration gradients. Moreover, this small fraction of Ni atoms might be poisoned by carbon impurities.

Ellipsometric measurements show that the initial oxygen uptake of Cu(100) with Ni up to $\delta \psi$ values of 0.7°, proceeds as with pure Cu(100). This implies that the Ni atoms in subsurface layers are not affecting the initial interaction with oxygen. At higher exposures, however, marked deviations from the behaviour of

pure Cu(100) are observed: ellipsometry shows at comparable exposures a substantially larger oxygen uptake than pure Cu(100). It can be seen from table 1 that after an oxygen adsorption leading to $\delta \Delta \simeq 1.7^{\circ}$, the 848 eV signal is attenuated much more than the Cu 920 eV peak. Apparently Ni facilitates the incorporation of oxygen into the lattice. At least some of these incorporated oxygen atoms are situated on top of the Ni atoms, which leads to a drop of the Ni Auger signal.

The reaction of CO with oxygen preadsorbed on Cu(100)—Ni is completely different from that on pure Cu(100) (see fig. 5) and also from that on pure Ni(100); oxygen adsorbed on pure Ni(100) does not react at all with CO [21]. Moreover, a residual amount of oxygen remains, even after prolonged CO exposures. After more oxidation—reduction cycles the amount of oxygen observed ellipsometrically rises (see table 1) much more steeply than the amount of oxygen measured with AES. Since ellipsometry probes much deeper into the crystal than Auger electrons do, this provides further evidence for nickel atoms facilitating the diffusion into the crystal. Accordingly a sputter profile showed oxygen remaining after extended sputtering times.

5. Conclusion

The above results lead to the following picture of oxygen sorption on Cu(100)— Ni prepared via dissociation of Ni(CO)₄: the first stage of oxygen adsorption proceeds as on pure Cu(100). At higher exposures oxygen is incorporated into the lattice at or near the Ni atoms. The oxygen taken up cannot be completely removed by reaction with CO. The Ni layer facilitates the penetration of oxygen and the diffusion but prohibits the complete reduction while the position of the layer of Ni atoms does not seem to change markedly after oxygen adsorption and reduction cycles.

Acknowledgements

The authors wish to thank Mr. A.H.J. Huijbers for technical assistance. The investigations were supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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