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Photoemission study of formation and oxidation of a cerium-copper interface

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Deposition of Ce on a polycrystalline Cu film has been studied by x-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy with use of synchrotron radiation. The formation of a relatively thick interface, > 100 Å, is observed at room temperature. The interface is found to contain about 80 at. % Ce and cannot be accounted for in terms of formation of an intermetallic compound based on the Ce-Cu phase diagram. A conversion from trivalent to tetravalent Ce ions is observed for a thin Ce-Cu interface when exposed to oxygen. The Cu substrate is not oxidized appreciably for oxygen exposures up to 1000 langmuir.

Metal overlayer systems have been given considerable attention from surface scientists over the past several years. The many observations of modifications in the electronic structure as well as in chemical reactivity at surfaces have triggered this interest. Of particular relevance for the present study are rare-earth overlayer systems. Recent measurements have shown that thin cerium overlayers have profound effects on the oxidation of substrates like Nb,[1] Ta,[2] Si,[3] and Al.[2,4] In the first two systems Ce forms an overlayer, and the observed enhancements in substrate oxidation rates are related to a conversion from tetravalent to trivalent Ce oxide.[1] In the latter two systems, enhancements in the oxidation rates are related to formation of a mixed interface region.[2–4]

The question of how an evaporated element goes down on a surface is of importance for the understanding of phenomena that occur at surfaces and interfaces. The possible fates of the deposited material may coarsely be grouped in three categories. First, a homogeneous overlayer may form; second, nucleation may occur at the surface; and third, the two elements may mix and form an interface compound or alloy.

If the surface energy,[5] or surface tension, of the deposited metal is considerably smaller than that of the substrate, one may expect a homogeneous overlayer to form.[6] On the other hand, if the surface energy of the evaporated material is larger than the substrate surface energy, the lowest-energy state may be one where the deposited atoms nucleate on the surface.[6] Then, there is the possibility that the energetically most favorable state is one where an interface alloy or compound has formed. Due to the complexity of this problem it seems nontrivial to predict the behavior of a given metallic overlayer system. In the present work, we have investigated the Ce on Cu system and have observed formation of a relatively thick, > 100 Å, intermetallic interface region. In addition, a thin Ce-Cu interface has been exposed to oxygen in order to obtain information on oxidation mechanisms.

The concept of surface energy is clearly not sufficient to predict the behavior of a given overlayer system. However, in the case of cerium being the deposited material, we make the following observations comparing recent experimental data with a compilation of surface tension data.[7] In some cases, where the surface tension of the substrate material is much higher than that of the deposited material, e.g., Nb and Ta, an overlayer is formed.[1,2] In other cases, where the substrate surface tension is similar to or a little larger than that of cerium, e.g., Al, Si, and Cu, surface alloys seem to form.[2–4]

These measurements were in part performed in the home laboratory and in part at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, beam line U7B. At home, the x-ray photoelectron spectra were recorded using a Vacuum Science Workshop (VSW) HA50 electron energy analyzer in conjunction with a VSW twin anode x-ray source. Beam line U7B at NSLS features a plane grating monochromator and was equipped with a VSW HA100 electron energy analyzer. An energy resolution of about 0.5 eV was obtained at a photon energy of 120 eV. In addition, an x-ray source (Al anode) from Physical Electronics was mounted on the chamber in order to monitor deep core levels. A resolution of near 1 eV was obtained in the x-ray photoelectron spectroscopy (XPS) spectra. All photoelectron spectra were recorded in the angle-integrating mode on polycrystalline samples. The samples were prepared by evaporation from tungsten baskets onto Ta foils that were attached to cryostats which could be cooled with liquid nitrogen. Cu films of thicknesses greater than 300 Å were used to mimic copper substrates. Thicknesses of evaporated metal layers were estimated from analysis of XPS core-level intensities.

An intensity analysis of cerium and copper core levels during deposition of Ce on a polycrystalline film of Cu at room temperature reveals that an interface alloy forms. Attenuation of the Cu $2p$ emission, as well as the increase in the Ce $3d$ emission with Ce evaporation at room temperature, are plotted in Fig. 1. Very similar results were obtained at a temperature of 0 °C. The effective Ce evaporation rate was estimated at about 5 Å/min on a noninteracting substrate, e.g., tantalum. An exponential attenuation curve that would be expected for deposition of a homogeneous overlayer is shown in Fig. 1. The observed deviation from the exponential curve is taken as evidence for formation of a surface alloy. It cannot be explained by aggregation of atoms on the surface, consid-

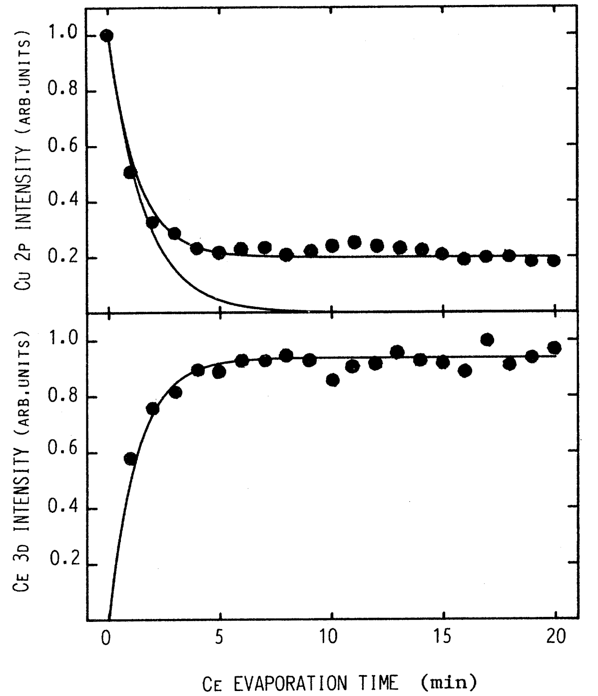

FIG. 1. Upper panel: Attenuation of Cu $2p_{3/2}$ intensity with Ce deposition on a Cu film. The effective Ce evaporation rate is 5 Å/min. The top line is a fit to the data as described in text. The bottom line shows exponential attentuation. Lower panel: Ce $3d_{5/2}$ intensity versus Ce deposition, solid circles. The line is a fit as described in text.

ering the relatively large extension of the flat region in Fig. 1, which corresponds to an effective overlayer thickness of more than 100 Å. Observations at liquid-nitrogen temperature show exponential attenuation of the Cu $2p$ intensity, thus indicating that alloying is suppressed. The measured intensities can be modeled fairly well by a simplified description in which a homogeneous mixed Ce-Cu interface layer on top of a Cu substrate is assumed. This description gives the following relation for the relative attenuated intensity of the Cu emission:

$$I_{\mathrm{Cu}}=(1-\alpha)+\alpha\exp(-tr/l\alpha)$$

where α is the volume fraction of Ce in the homogeneous overlayer, t and r are Ce evaporation time and rate, respectively, and l is the electron mean free path for Cu $2p$ emission (and for Ce $3d$ emission). The relationship between the Ce $3d$ photoemission intensity and Ce evaporation time in this model can be written as

$$I_{\mathrm{Ce}}=A[1-\exp(-tr/l\alpha)]$$

where A is a scale factor which is adjusted to fit the data. The data are fitted by using parameters $\alpha=0.8$, $r=5$ Å/min, and $l=8$ Å; solid lines in Fig. 1. The value of $\alpha=0.8$ indicates that the interface, on the average, contains nearly 80 at. % Ce. The absence of Ce-rich compounds in the Ce-Cu phase diagram[8] bears evidence that an interface alloy has been formed in this metallic overlayer system. Recent work on the Yb-Cu system[9] also shows that room-temperature alloying takes place, which is consistent with the present work, considering the relative chemical similarities of the lanthanide elements.

Valence-band photoemission spectra show a narrowing of Cu $3d$ emission when Ce is deposited on the surface. The spectral weight of the emission is also shifted to higher binding energies. This is shown in the case of an effective Ce deposition of about 5 Å in Figs. 2(a) and 2(b). These effects are likely to be caused by hybridization between copper $3d$ and cerium $4f$ states. The Ce $4f$ emission can be resonantly enhanced by tuning the photon energy to the super-Coster-Kronig transition[10] of 122 eV for Ce, Fig. 2(c). By subtracting the off-resonance spectrum (112 eV) from the on-resonance spectrum (122 eV), we obtain the $4f$ emission, Fig. 2(d). The off-resonance curve has been scaled so that the Cu $3d$ emission is subtracted out of the difference curve. Two contributions to the $4f$ emission are observed; the peak near a binding energy of 2 eV corresponds to direct photoexcitation of a $4f$ electron, whereas the one near the Fermi level has been previously attributed to a final-state screening process.[11,12] The $4f$ emission spectrum resembles that of Ce in its trivalent state.[13] The absence of a $4f^0$ peak near

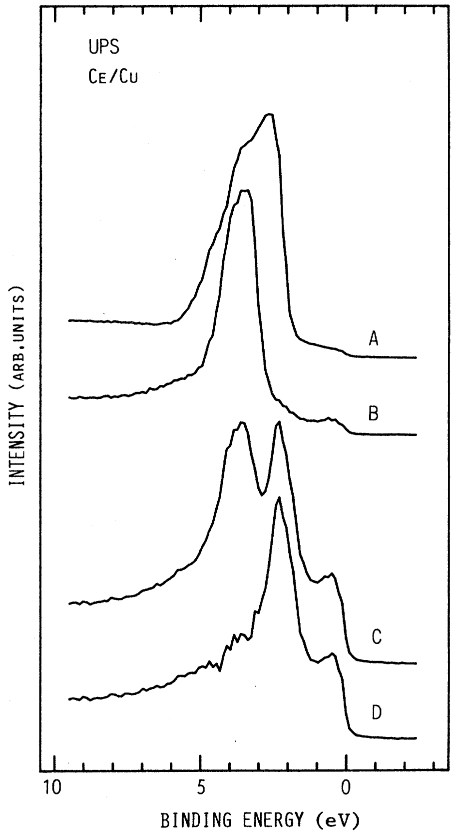

FIG. 2. Valence-band photoelectron spectra. A: Evaporated copper film at a photon energy of 112 eV. B: 5 Å effective Ce deposition on Cu, taken at 112 eV (off resonance). C: Same as B at 122 eV (on resonance). D: Ce $4f$ emission spectrum, i.e., difference curve between spectra C and B. Curve B has been scaled to minimize Cu $3d$ emission in the difference curve.

917 eV in the Ce 3*d* core-level emission, shows that Ce ions in the Ce-Cu interface are in their trivalent state, top curve in Fig. 3. The feature near 925 eV in this curve is an artifact caused by the presence of the Al $K\alpha_{3,4}$ satellite in the exciting radiation.

Part of the motivation for the present experiment was, based on earlier observations on rare-earth overlayer systems,[1-4] to investigate possible effects of a Ce overlayer on oxidation of a copper substrate. Copper 2*p* and cerium 3*d* spectra are shown for various oxygen exposures in Fig. 3. The top curve represents the unoxidized Ce/Cu system, whereas the remaining spectra shows oxygen exposures from 2 to 100 L (1 $\mathrm{L}=10^{-6}$ Torr sec). The 2- and 5-L spectra exhibit the four Ce 3*d* peaks characteristic of trivalent Ce oxide.[14] These spectra contain contributions from metallic peaks as well. At an oxygen exposure of about 10 L, tetravalent Ce oxide is observed, as indicated by the appearance of a peak near 917 eV and also by the overall changes in the 3*d* emission. Eventually, at exposures above 100 L, the Ce 3*d* spectrum is characteristic of $\mathrm{CeO_2}$.[15] The Cu $2p_{3/2}$ peak shows only minute shifts in position upon oxidation. The most interesting information obtained from these core-level spectra seems to be related to the conversion from trivalent to tetravalent Ce ions during the oxidation of the sample. It has previously been noted that intermetallic compounds based on Ce tend to form trivalent oxides.[3] Formation of tetravalent oxide in the present experiment thus seems to corroborate the conjecture of a Ce-Cu alloy.

Valence-band spectra taken at the super-Coster-Kronig resonance energy of 122 eV show that the 4*f* emission is attenuated when the system is oxidized, Fig. 4. However, even after an oxygen exposure of 500 L, some 4*f* emission remains, as seen by the presence of the peak at a binding energy of about 2 eV in the bottom curve. This resonant photoemission technique provides a more sensitive probe for *f* emission than deep core-level spectroscopy, Fig. 3, which showed a spectrum characteristic of tetravalent Ce oxide already after an exposure of 100 L. Still, the oxide film contains predominantly tetravalent Ce ions for oxygen exposures of above 100 L. In the top spectrum in Fig. 4, the Cu 3*d* emission is present together with the two 4*f* peaks at lower binding energies. The copper peak is completely suppressed after an exposure of only 2 L. At this stage only the O 2*p* features in the region 4–7 eV and the Ce 4*f* line near 2 eV are present. The oxygen 2*p* peak that emerges near 4 eV is characteristic of tetravalent Ce oxide. A small shift of the major 4*f* peak to

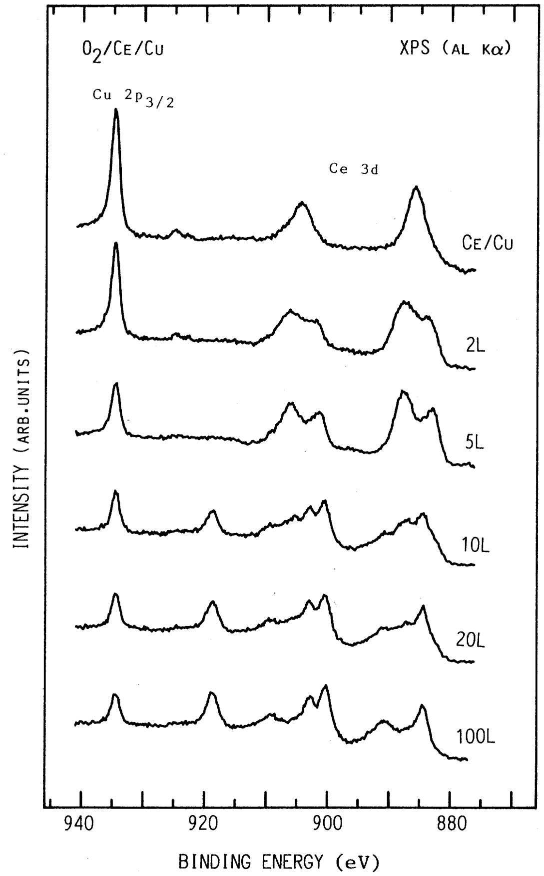

FIG. 3. X-ray photoelectron spectra showing the region of the Cu $2p_{3/2}$ and the Ce 3*d* peaks of the Ce/Cu system. Various oxygen exposures are indicated in the figure. The effective Ce evaporation is 5 Å.

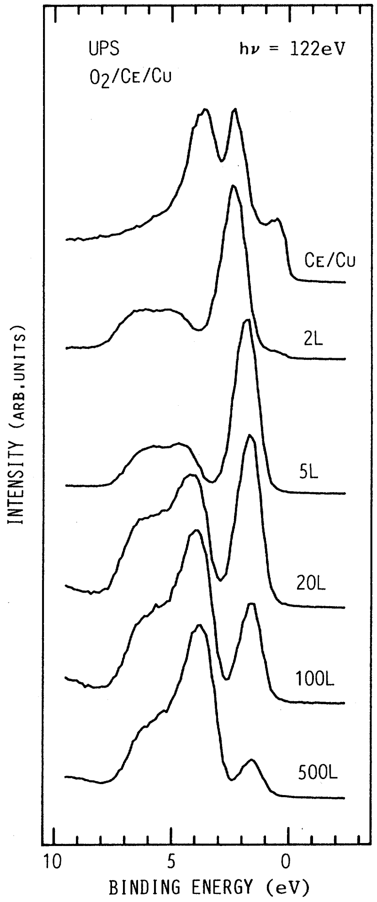

FIG. 4. Valence-band spectra of the Ce/Cu system. Oxygen exposures are indicated. The effective Ce thickness is 5 Å. The photon energy is the super-Coster-Kronig resonance energy of 122 eV to enhance Ce 4*f* emission.

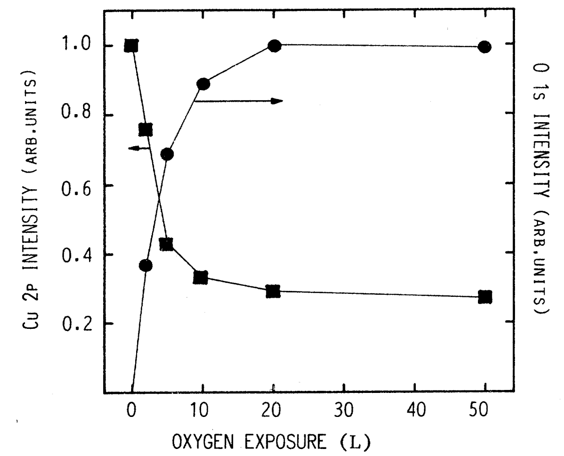

FIG. 5. Squares, attenuated Cu $2p_{3/2}$ emission intensity vs oxygen exposure to the Ce/Cu system; circles, corresponding increase in oxygen 1*s* emission. Lines are guides to the eye. The effective Ce deposition is 5 Å. The oxygen uptake is strongly reduced after about 20 L.

lower binding energy, which may be related to final-state screening effects, is observed with oxygen exposure.

Only the mixed interface is oxidized. For the effective Ce evaporation of 5 Å as presented in this work, the amount of oxygen increases up to an exposure of 20 L. After this point the O 1*s* as well as the Cu 2*p* intensities stay unchanged, Fig. 5. Thus the mixed overlayer does not enhance oxidation of the substrate. This finding is corroborated by the absence of a Cu^{2+} peak in the Cu 2*p* emission. However, presence of Cu^{1+} cannot readily be observed in low-resolution XPS due to the minute size of the chemical shift.

In conclusion, we have observed the formation of a mixed Ce-Cu interface when Ce is evaporated on a polycrystalline copper film at room temperature. The growth of this interface proceeds to form a more than 100-Å-thick layer as Ce is deposited. Oxidation of a thin interface (5 Å effective Ce deposition) results in a conversion from trivalent to tetravalent Ce ions. At an oxygen exposure of 500 L, tetravalent Ce oxide prevails in the interface. The copper substrate is not oxidized at an appreciable rate for exposures up to 1000 L. This work may have some bearing on studies of thin rare-earth overlayers, e.g., two-dimensional magnetic systems, where ordered overlayers are sought.

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[1] E.-E. Latta and M. Ronay, Phys. Rev. Lett. **53**, 948 (1984); M. Ronay and E.-E. Latta, Phys. Rev. B **32**, 5375 (1985).

[2] N. A. Braaten, J. K. Grepstad, and S. Raaen, Surf. Sci. (to be published).

[3] F. U. Hillebrecht, M. Ronay, D. Rieger, and F. J. Himpsel, Phys. Rev. B **34**, 5377 (1986).

[4] S. Raaen, N. A. Braaten, J. K. Grepstad, and S. L. Qiu, Phys. Scr. (to be published).

[5] The surface energy may be defined as the excess internal energy of the solid-vacuum system over that of an imaginary system with two homogeneous phases separated by an ideally discontinuous change at a mathematical surface between them; see, e.g., J. M. Blakely, *Introduction to the Properties of Crystal Surfaces* (Pergamon, Oxford, 1973).

[6] See, e.g., M. Prutton, *Surface Physics* (Clarendon, Oxford, 1983).

[7] See, e.g., A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, England, 1988).

[8] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).

[9] V. Murgai and Young-Sea Huang, Bull. Am. Phys. Soc. **34**, 800 (1989); (unpublished).

[10] F. Gerken, J. Barth, and C. Kunz, in *X-ray and Atomic Inner-Shell Physics* (*University of Oregon, Eugene, Oregon, 1982*), Proceedings of the International Conference on X-Ray and Atomic Inner-Shell Physics, AIP Conf. Proc. No. 94, edited by B. Crasemann (AIP, New York, 1982), p. 602.

[11] P. S. Riseborough, Solid State Commun. **57**, 721 (1986); J. Magn. Magn. Mater. **47&48**, 271 (1985).

[12] R. D. Parks, S. Raaen, M. L. denBoer, Y. S. Chaug, and G. P. Williams, Phys. Rev. Lett. **52**, 2176 (1984).

[13] N. Mårtensson, B. Reihl, and R. D. Parks, Solid State Commun. **41**, 573 (1982).

[14] J. C. Fuggle, M. Campagna, Z. Zołnierek, R. Lässer, and A. Platau, Phys. Rev. Lett. **45**, 1597 (1980).

[15] E. Wuilloud, B. Delley, W.-D. Schneider, and Y. Baer, Phys. Rev. Lett. **53**, 202 (1984).