XPS STUDIES OF THE OXIDATION OF U-SI COMPOUNDS

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XPS studies of the oxidation of U_3 Si, USi ₂, and USi₃ have shown very similar oxidation behavior for both constituents. Moreover, the oxidation rate in both U- and Si-related signals is found to increase with increasing uranium concentration. The results are interpreted in terms of a combined oxidation of U-Si complexes

1. Introduction

The chemical reactivity of metal/semiconductor interfaces is an important factor in the quality control of microelectronic devices, and a large amount of research activities is presently being devoted to that topic [1]. Even though these are not very likely to include interfaces with actinide elements, a detailed understanding of their properties is nevertheless very important to gain some insight into the parameters that control these properties. Moreover, oxidation and corrosion phenoma of actinide compounds have an immediate relevance to waste-storage management. Due to the difficulty in handling radioactive materials, so far uranium is the only element on which several studies have been reported. These have shown a drastic variation of oxidation properties between different compounds, which have been attributed either to differences in the bonding between U and the partner element, or to diffusion and surface segregation properties based on geometric differences [2,3]. To serve both lines of interest, we have investigated the oxidation of U-Si rich compounds with relative U: Si concentration of 3, 1, 0.5, and 0.33 (i.e. U₃Si, USi, USi₂, and USi₃) using X-ray photoelectron spectroscopy.

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2. Experimental

The samples were prepared by melting the constituents in an inductionheated levitation crucible under Ar atmosphere and characterized by metallography and X-ray diffraction. They were cleaned in situ by scraping with a ceramic file under UHV conditions $(10^{-10} \text{ Torr range})$. Photoelectron spectra were recorded in a custom-built spectrometer equipped with a large solid-angle monochromator for Al K α radiation [4], having a total resolution of 0.7 eV. Contamination was controlled by monitoring the O1s and C1s signals. We also checked the (XPS-derived) U and Si surface concentration from the ratio of the U4f versus Si2s signals of the clean compounds. Using this ratio for USi to calibrate for the cross section differences we obtained U: Si ratios of 0.34, 0.54, and 3.5 for USi₃, USi₂, and U₃Si, indicating no significant surface segregation. Oxygen exposures were carried out at room temperature and at oxygen partial pressures in the 10^{-8} - 10^{-6} Torr range.

3. Results

Fig. 1 shows the U4f spectra of the four compounds at increasing oxygen exposure. In each case, the $U4f_{7/2}$ peak of the clean compound appears at 377.3 ± 0.1 eV with respect to $\vec{E}_{\rm F}$, with a spin-orbit splitting between the $U4f_{7/2}$ and $U4f_{5/2}$ peaks of 10.6 \pm 0.1 eV. Upon oxidation, a pair of peaks shifted with respect to the original ones by about 3.3 eV developes at the expense of the latter. This happens more or less rapidly for USi₂, USi, and U₃Si, but only slowly for USi₃. In order to identify the oxide species involves, we have presented the difference spectra of the partially oxidized and clean sample for the case of U_2 Si together with the corresponding spectrum of a UO₂ single crystal [5] in fig. 2. To align the spectra, only the UO₂ spectrum had to be shifted by 0.7 eV towards higher binding energy, which is attributed to the different reference energies chosen in the energy calibration ($E_{\rm F}$ of the clean compound for the $U_x Si_y$ versus E_F of a gold overlayer for UO₂). The difference spectra of the other three compounds look exactly the same and show the same $U4f_{7/2}$ binding energy within 0.1 eV. It is evident from the line shape that only one oxide species is formed at all stages and for all compounds. The binding energy of this oxide is similar to that of UO₂. However, it is significant to note that the separation of 6.4 eV between the satellite and main line in this case is considerably different from that of the characteristic satellite in UO_2 (6.8 eV) [5,6].

Fig. 3 shows the Si2s spectra of the four compounds as a function of exposure. Due to the small cross section and the high tendency to contamination, which limits the counting time, it is difficult to obtain good statistics for these spectra, and in the case of the two samples with the smallest Si





Fig. 1. X-ray photoelectron spectra of the U 4f levels of (a) USi₃, (b) USi₂, (c) USi, (d) U₃Si after exposure to increasing amounts of oxygen.

Fig. 2. Difference between the U 4f spectra of the partially oxidized and clean U_3Si samples of fig. 1 and of UO_2 for comparison. The spectrum of UO_2 is from ref. [5] and has been shifted by 0.7 eV towards higher binding energy.

concentration, USi and U_3Si , they have been smoothed for clarity of the picture. Unfortunately, Si 2p spectra, which have been thoroughly investigated for pure Si, are not very useful for U-Si compounds, as they overlap with the 5d spectrum of U. Nevertheless, some very interesting qualitative and semi-



Fig. 3. X-ray photoelectron spectra of the Si2s level of (a) USi_3 , (b) USi_2 , (c) USi, (d) U_3Si after exposure to increasing amounts of oxygen. The solid lines indicate the Si2s binding energies for the clean and oxidized samples observed in this work, and the dashed lines mark the corresponding binding energies for Si bonded to 1, 2, 3, or 4 O atoms as observed on the oxidized Si(100) and (111) surfaces [7].

quantitative conclusions can be drawn from the spectra presented here. First, the fact that Si does oxidize in these compounds, and in most samples even quite strongly, is not at all a triviality. It is in fact in clear contrast to the slow



Fig. 4. Ratio of the oxide to pure compound intensity for $U_x Si_y$ as a function of exposure. (a) U4f signal, (b) Si 2s signal. The corresponding values for U and Si have been obtained from refs. [9,7] respectively. c = x/y indicates the relative uranium concentration.

oxidation found in pure Si [7], and to the observations at the Ti/oxygen/Si interface, where Ti is actually found to reduce the existing silicon oxide [8]. Second, a comparison with the 2s photoemission data of oxidized clean single crystal silicon [7], indicated by the dashed lines, suggests that the present oxide consists predominantly of SiO₃ units, assuming the chemical shift for the 2s and 2p levels to be roughly the same. Even though it is hard to determine from the quality of the present data, whether this is the only oxide species formed, they do not support a distribution with roughly equal intensity over all four oxidation states, as reported by Hollinger et al. [7]. Moreover, and again within the uncertainty of the data, there is no indication for a change of oxidation state with exposure or from one compound to the other. Third, as in the case of the U4f spectra, the samples with higher U concentration. This

can be seen qualitatively from the reversal of intensity ratios of the clean and oxide Si 2s peaks at 50 L exposure as the relative U concentration is changed. It is shown more quantitatively in fig. 4, which shows the ratio of the oxide to pure compound intensity for both the U4f and Si2s signals as a function of exposure. In the case of the U4f signal they have been obtained from the area under the oxide and clean compound contribution to the total spectrum after appropriate curve separation. In the case of the Si 2s signal only the respective peak heights have been used because of the larger scatter of the data points. The corresponding values for the pure elements, U and Si, have been obtained from spectra reported in the literature [7,9]. Both U and Si show qualitatively the same behaviour, namely a high tendency towards oxidation for U₃Si, and a relatively strong oxidation resistance for USi₃. The situation for USi₂ and USi is intermediate between these two cases. The most striking result is that the oxidation rate of the compounds does not approach the oxidation rate of pure uranium as its concentration becomes preponderant. Instead, both elements are resembled closest by the oxidation behavior of USi₃, which shows the strongest oxidation resistance. This shows that the U-Si bonds are essential for the rapidity of the oxidation process, a point that will become more clear in the subsequent discussion of the oxidation mechanism.

4. Discussion of the oxidation mechanism

Let us first consider the origin for the different oxidation behavior of the U-Si compounds. Both USi₃ and U₃Si crystallize in the cubic Cu₃Au structure or in the body-centered tetragonal structure related to it. Moreover, the U4f and Si 2s binding energies of all four compounds vary by only 0.1 eV and



Fig. 5. Ratio of the total U4f versus Si2s signals of partially oxidized $U_x Si_y$ normalized to the relative uranium concentration (c = x/y) of the clean compounds.

0.3 ev respectively. The different oxidation behavior can therefore neither be attributed to crystallographic differences nor to modifications in the charge transfer between U and Si. Rather, the oxidation of U must lead to the breaking of some U-Si bonds, giving rise to "dangling bonds" of Si. This would explain the increased reactivity of Si in these compounds compared to pure Si. The shift of the U4f satellites with respect to the bulk UO₂ spectrum should be taken as an indication that the oxide of U in this case is not present in its pristine UO₂ form. We have also used the ratio of the U4f versus Si2s signals (clean and oxide contributions) to determine the relative uranium concentration in the surface layer sampled by our technique. The results normalized to the concentration of the clean compounds are presented in fig. 5. Except for a possible onset of surface segregation for USi₂ around 50 L, the U concentration is not significantly enhanced (less than 20%). This is different from what has been observed in other U compounds [3], and indicates that oxidation in the compounds studied here proceeds primarily via anionic oxygen diffusion rather than by cationic diffusion from the bulk. Under such circumstances, it is understandable that oxygen, while breaking the U-Si bonds, will react simultaneously with both U and Si. This is supported by the close parallel between the oxidation behavior of U and Si in each compound seen in fig. 4. The change in the satellite position compared to that in UO, is also indicative of such a combined oxidation. To our knowledge, this is the first experimental observation of such a coupled oxidation process.

5. Conclusion

The above results suggest that oxidation in each of the four compounds studied proceeds primarily via anionic oxygen diffusion rather than by cationic diffusion. Moreover, we find strong evidence for simultaneous oxidation of uranium and silicon in the form of a combined oxide rather than as separate oxides of U and Si. The fact that all compounds oxidize faster than either of the constituents implies that U–Si bonds are essential for the rapid oxidation. This means, that U–Si bonds are more readily broken by oxygen than either U–U bonds (as in pure U) or Si–Si bonds (as in pure Si). The remaining differences seen in the rapidity of oxidation between the four compounds studied must be due to differences in the details of geometry and bonding.

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References

- See, e.g. Proc. Intern. Conf. on the Formation of Semiconductor Interfaces, Marseille, 10-14 June 1985 [Surface Sci. 168 (1986)].
- [2] W.D. Schneider and C. Laubschat, Phys. Rev. B23 (1981) 997.
- [3] D.D. Sarma, F.U. Hillebrecht and M. Campagna, Surface Sci 162 (1985) 563.
- [4] J.C. Fuggle, E. Hanning and J. Keppels, to be published.
- [5] Y. Baer and J. Schoenes, Solid State Commun. 33 (1980) 885.
- [6] P.R. Norton, R.L. Tapping, D.K. Creber and W.J.L. Buyers, Phys. Rev. B21 (1980) 885.
- [7] G. Hollinger and F.J. Himpsel, J. Vacuum Sci. Technol. A1 (1983) 640.
- [8] R. Butz, G.W. Rübloff and P.S. Ho, J. Vacuum Sci. Technol. A1 (1983) 771.
- [9] J.C. Fuggle, A.F. Burr, L.M. Watson, D.J. Fabian and W. Lang, J. Phys. F4 (1974) 335.