Interaction of CO with $Cu_{50}Zr_{50}$ metallic glass surface[†]

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Abstract. The adsorption of CO has been studied on the surface of a $Cu_{50}Zr_{50}$ metallic glass using X-ray and ultraviolet photoelectron spectroscopic techniques. CO dissociates on both these surfaces leading to the formation of graphitic and carbidic carbon species on the surface. However a reversal in intensity of the two species is observed on the metallic glass surface compared to that on the Zr metal surface. While Zr gets oxidised due to the oxygen produced as a result of the dissociation of CO, Cu remains unoxidised.

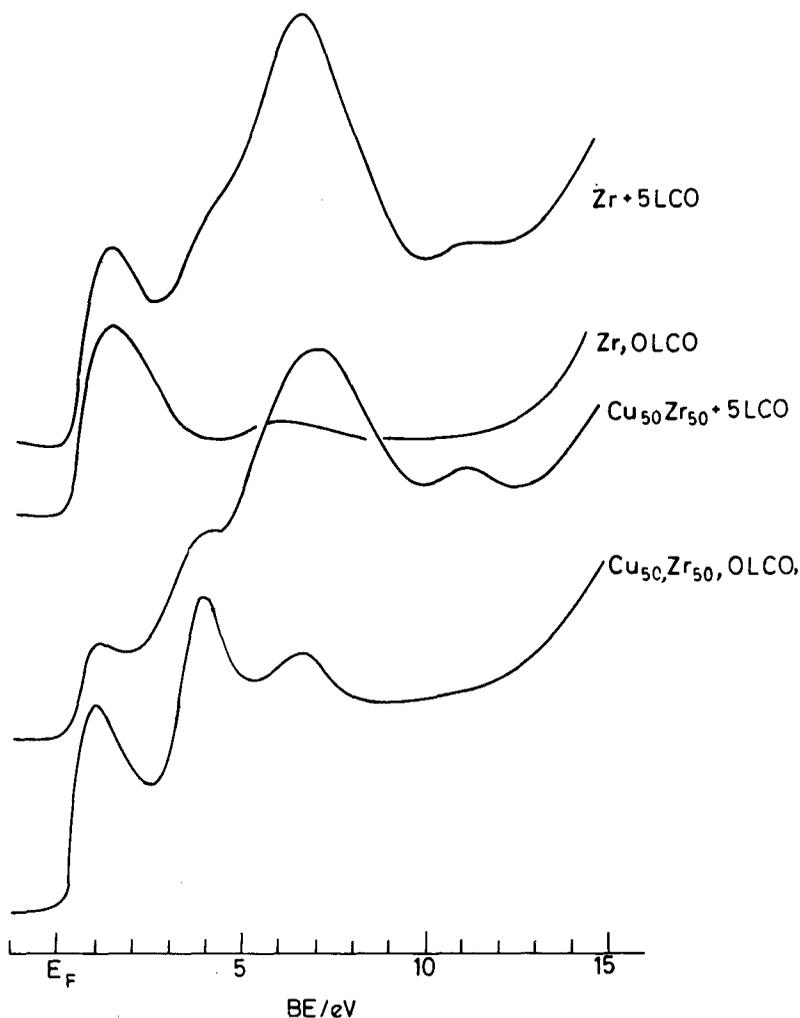**Keywords.** Metallic glass surface; photoelectron spectroscopy; adsorption of CO.

1. Introduction

Techniques of electron spectroscopy have been widely used to understand the electronic structure of metallic glasses (Oelhafen 1983). However there have been only few studies of the interaction of molecules with the surfaces of these novel materials (Prabhakaran and Rao 1985; Domanek *et al* 1985) directed towards understanding the catalytic activity of these materials (Kisfaludi *et al* 1985). It has been recently shown that metallic glasses are better catalysts than their crystalline counterparts. This has been attributed to their homogeneous nature, high concentrations of low coordination sites at their surfaces (Yoon and Cocke 1986). A surface oxidation study of these metallic glasses has revealed that amorphous ribbons behave differently compared to their crystalline counterparts (Sen *et al* 1984), the glassy alloys exhibiting a higher rate of oxidation at intermediate exposures of O_2. Adsorption of CO on well-characterized metal surfaces has been investigated extensively in the past several years (Engel and Ertl 1979). In certain industrially important reactions bimetallic catalysts are known to perform better than the individual metal catalysts (Sinfelt *et al* 1984). Adsorption characteristics and hence the catalytic properties are markedly affected upon alloying. There have been efforts to explain this in terms of the changes in the electronic structure. We have studied the interaction of CO with the surface of amorphous $Cu_{50}Zr_{50}$ alloy ribbon. We have employed X-ray photoelectron spectroscopy with facilities for *in situ* adsorption studies.

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2. Experimental

The X-ray and UV photoelectron spectroscopic measurements were carried out in a VG ESCA-3 Mark II spectrometer. The $Cu_{50}Zr_{50}$ alloy ribbon was mounted on a P8 probe where the sample could be cooled to liquid nitrogen temperature and heated to 800 K. The sample was cleaned by argon ion bombardment until the intensities of the $C(1s)$ and $O(1s)$ signals in the XPS were negligible. CO was prepared by the reaction between formic acid and sulphuric acid. It was dried over P_2O_5 and purified further using liquid nitrogen traps. Purity of the gas was checked with a quadrupole mass spectrometer. Vacuum in the spectrometer chamber was close to 10^{-10} Torr. The exposures of the gas are expressed in terms of Langmuirs $(1 L = 10^{-6}$ Torr.s).

Figure 1. HeII photoelectron spectra of $Cu_{50}Zr_{50}$ metallic glass surface and Zr metal surface before and after adsorption of CO at 300 K.

3. Results and discussions

Adsorption of CO on the Cu$_{50}$Zr$_{50}$ metallic glass was carried out at 300 K. HeII photoelectron spectra of CO on the Cu$_{50}$Zr$_{50}$ and Zr metal are given in figure 1. The spectra clearly show dissociation of the molecule leading to the formation of carbon and oxygen on both these surfaces. The broad feature covering the region 6–10 eV is due to the oxide and carbide layers. The small feature at 11 eV will be discussed at a later stage. The C(1s) region shows two distinct peaks at 282·3 and 285·5 eV which are assigned respectively to carbidic and graphitic carbons. The appearance of two types of carbon species on metal surfaces has been reported in the literature. For example, Load and Reveire (1971) have found that on a Ni surface, carbon exists in carbidic as well as graphitic forms. Similar observations have been reported on Ni(110) (McCarty and Madix 1976), Zr (Craig *et al* 1983), Ru(101) (Papagno *et al* 1983). Another study (Kelley and Grobman 1982) on catalytic methanation over single crystal Ni and Ru has correlated the surface carbide concentration with reaction rate. They have concluded that the methanation reaction rate is determined by a delicate balance between the formation and removal of surface carbide. It has been experimentally demonstrated that for CO on several transition metals (Ru, Ni, Fe), a surface form of carbidic carbon is an intermediate in the Fischer-Tropsch synthesis (Kelley and Grobman 1980). The surface population of both carbidic and graphitic species increases on increasing the exposure of CO (figure 2).

In figure 2, we have also shown the C(1s) spectra of CO adsorbed on clean Zr. The spectra show the presence of two distinct peaks at 282·3 and 285·5 eV due to carbidic and graphitic species, respectively. The intensity of the peak due to the graphitic carbon is lower than that due to carbidic carbon. This reversal in population of the two carbon species on the Zr metal surface (compared to the Cu$_{50}$Zr$_{50}$ surface) can only be due to differences in the two surface resulting from alloying and possibly due to the amorphous nature of the alloy. The O(1s) region shows a single peak at 531·1 eV due to oxidic oxygen on both Cu$_{50}$Zr$_{50}$ and Zr surfaces (figure 3).

The Zr(3d) level shows interesting changes on exposure of CO. Zr undergoes extensive oxidation to give various oxides ZrO, ZrO$_2$ (figure 4) on the surface whereas the Cu remains unchanged. The Cu(2p) level shows no changes in line shape. In the case of Cu$_{50}$Zr$_{50}$, the Zr(3d$_{5/2}$) at 178·6 eV and (3d$_{3/2}$) levels at 180·9 eV shift to 182·4 and 184·7, respectively. This 4 eV shift as well as a comparison of the spectrum with that of the bulk oxide suggests the formation of ZrO$_2$. To ascertain the nature of the oxide species at high exposures of CO we have decomposed the 3d peak of Zr in terms of contributions from clean Zr and bulk ZrO$_2$ by a least squares fitting procedure (figure 5). From the figure it is clear that the contributions of both Zr and ZrO$_2$ are overestimated leading to negative error values in the respective ranges. Moreover part of the intensity (in between the peaks due to Zr and ZrO$_2$) is not accounted for in this fitting procedure, suggesting the presence of an oxide of Zr with a lower oxidation number than in ZrO$_2$. Assuming that this lower oxide of Zr has a similar 3d line shape as in ZrO$_2$ but shifted in energy, we have analysed the 3d spectrum following the procedure described in an earlier paper from this laboratory (Sen *et al* 1984). The results yield uniformly low errors, indicating that this second oxide species should be taken into
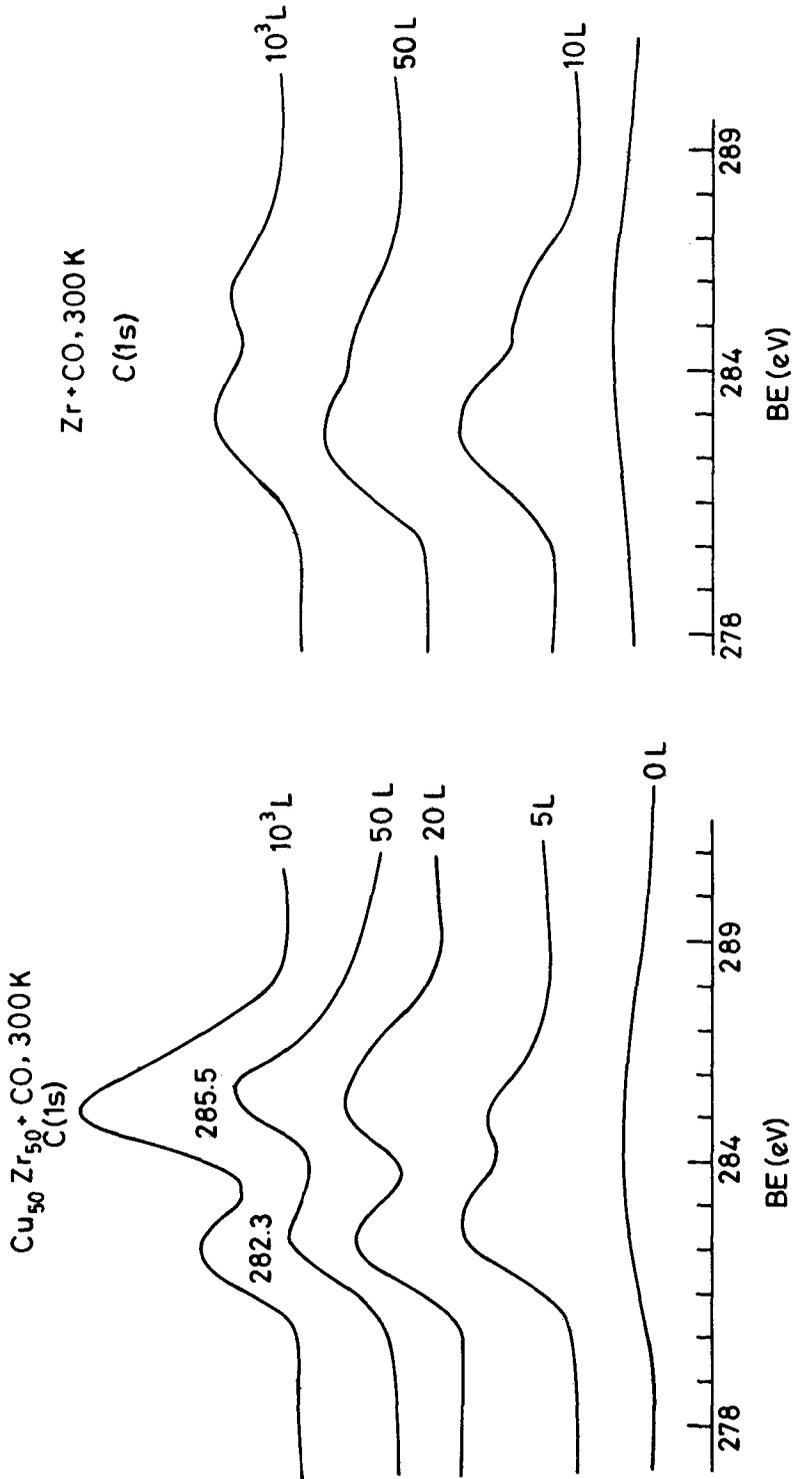
Figure 2.   X-ray photoelectron spectra in the C(1s) region at various exposures of CO on the $Cu_{50}Zr_{50}$ metallic glass surface and Zr metal surface.
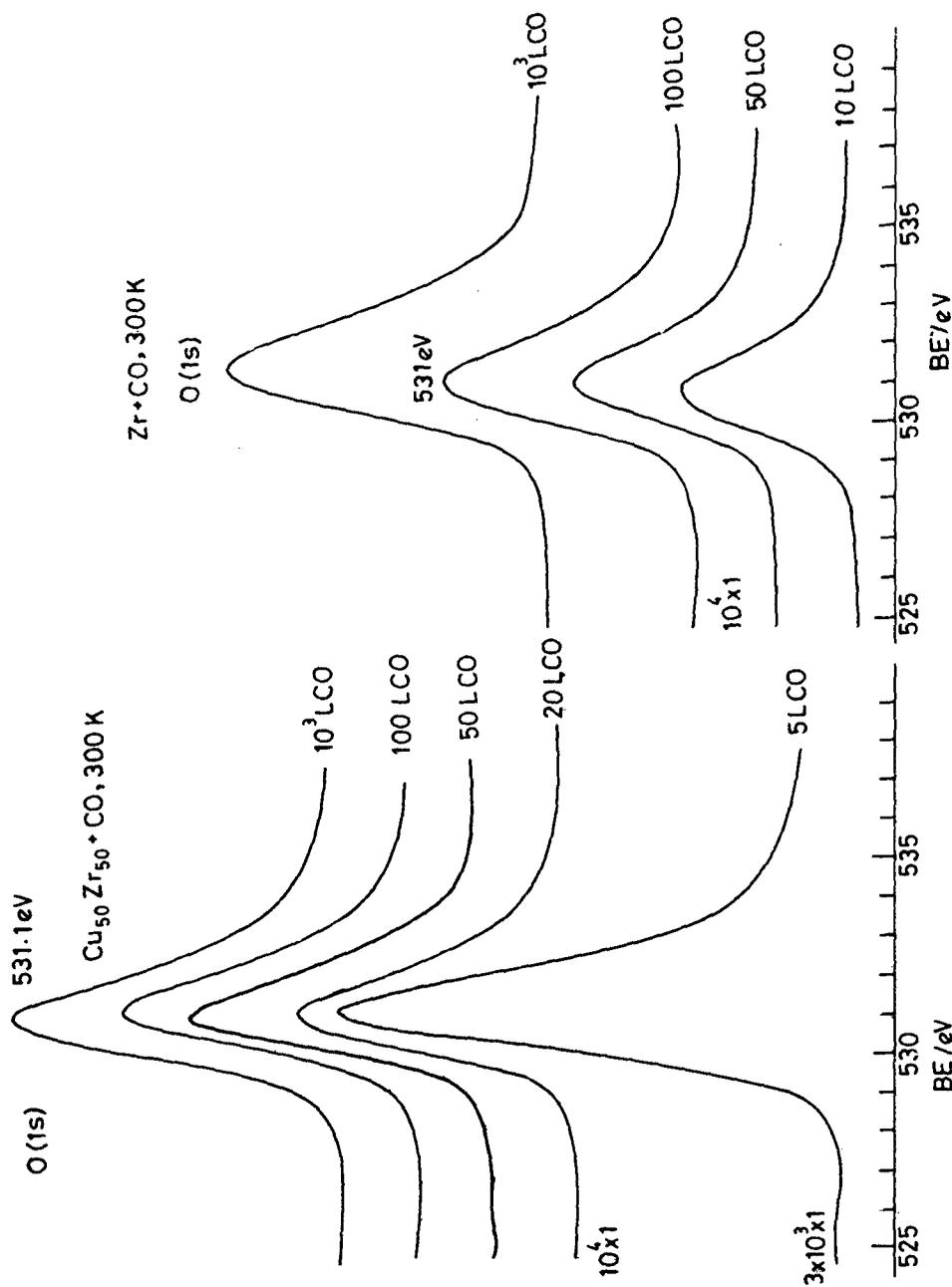
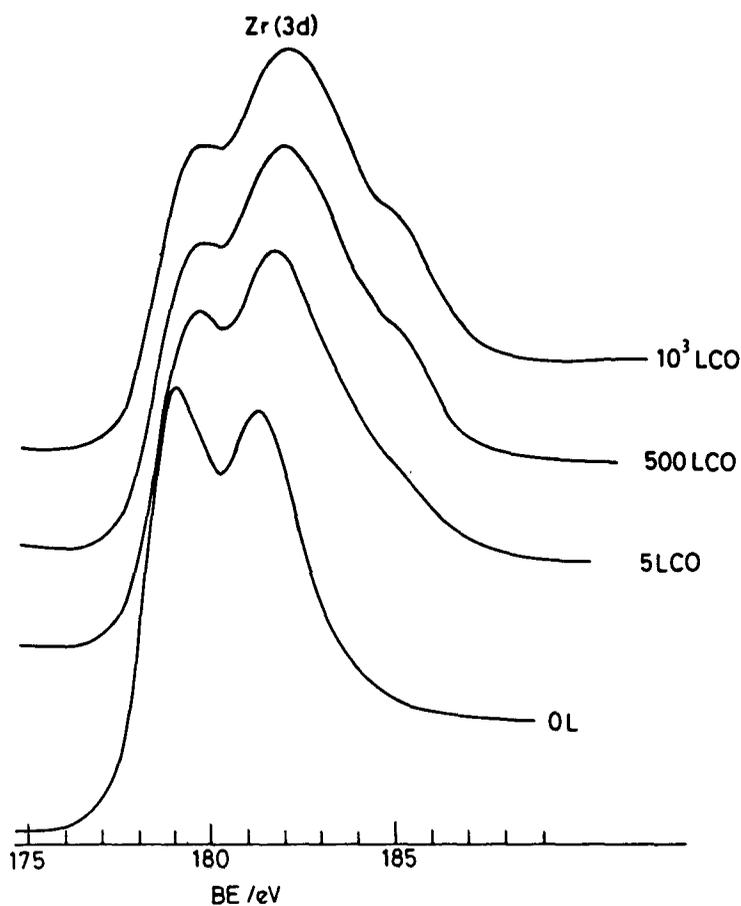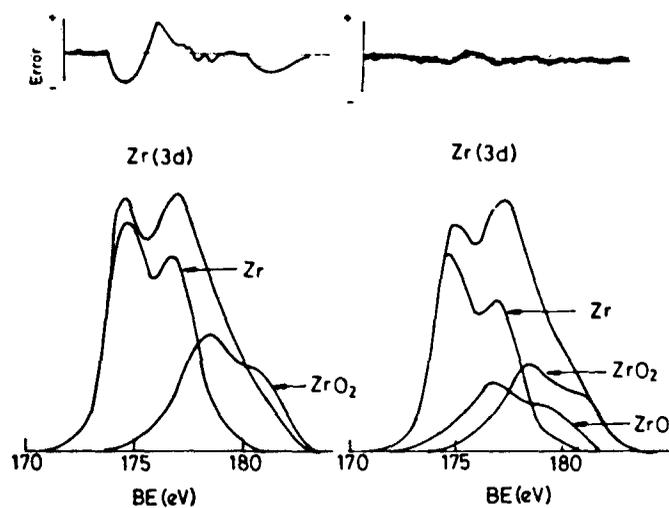**Figure 3.** X-ray photoelectron spectra in the O(1s) region at various exposures of CO on the Cu₅₀Zr₅₀ metallic glass surface and Zr metal surface.

Zr(3d)

10^3 LCO

500 LCO

5 LCO

OL

175   180   185

BE /eV

Figure 4. X-ray photoelectron spectra in the Zr(3d) region at various exposures of CO on the Cu$_{50}$Zr$_{50}$ metallic glass surface.

Error

Zr(3d)   Zr(3d)

Zr   Zr

ZrO$_2$ ZrO$_2$

                           ZrO

170   175   180   170   175   180

BE (eV)   BE (eV)

Figure 5. Decomposition of the Zr(3d) spectrum of the Cu$_{50}$Zr$_{50}$ + 5LCO into various components using the least squares fit method.

account to explain the broadening of the $3d$ level. Many suboxides are known in the bulk (Rao and Rao 1974) and the formation of these suboxides on the surface had been suggested by Foord *et al* (1986). The highest suboxide reported in the literature is ZrO_2. We find that as the CO exposure increases the chemical shift of the suboxides keeps increasing attaining a stable state at 10 L. The $Zr3d$ spectrum corresponding to 10 L CO exposure shows evidence for the presence of an oxide with approximately 2 eV chemical shift as shown in figure 4 together with the ZrO_2 (4 eV chemical shift). The binding energy of the oxide species with 2 eV chemical shift lies exactly between Zr and ZrO_2. We suggest that the composition of the surface oxide corresponds to the highest possible suboxide which is ZrO.

The feature around 11 eV in the UPS (figure 1) cannot be due to molecular adsorption of CO because the corresponding $O(1s)$ spectrum shows a single peak at 531·1 eV characteristic of an oxidic species resulting from dissociated CO. In order to ascertain this observation we have carried out an independent oxygen adsorption study of the $Cu_{50}Zr_{50}$ metallic glass and Zr metal. Figure 6 shows the UPS of oxygen adsorption at 80 K. The oxygen molecule instantly dissociates and Zr gets oxidised even at low temperatures. The spectrum shows a broad band covering the region 6–10 eV and a small feature at 11 eV. The $O(1s)$ spectrum shows a single peak at 531 eV. We therefore feel that the feature at 11 eV is due to some satellite arising out of the surface oxide. The possibility that the feature at 11 eV in the case of dissociative adsorption is due to the graphitic carbon cannot be ruled out. This is because the valence band of graphite also shows a feature in this region (Bianconi *et al* 1977).

The difference with respect to the adsorptive characteristics of CO on $Cu_{50}Zr_{50}$ metallic glass compared to Zr metal can be understood in terms of the alteration in the electronic properties. The Cu-derived d states shift towards higher binding energies in the metallic glass thereby enhancing the contribution of the Zr derived d states to the total density of states at E_f. It is noteworthy that on a $Cu_{70}Zr_{30}$ metallic glass (we could not remove the contaminant oxygen completely) CO dissociates to give only one type of carbon species, i.e., graphitic carbon with $C(1s)$ at 285·7 eV.

At this stage it is difficult to predict the catalytic activity of these Cu-Zr metallic glasses. However the presence of carbidic carbon which is crucial for the catalytic reactions is promising. On argon ion bombardment and subsequent heating to 350 K, the carbidic carbon alone was formed on the surface. This means that segregation of carbidic carbon alone on the surface occurs on replenishment of the carbidic carbon already present on the surface. On a Zr metal surface this does not happen. This suggests that these metallic glasses may be good catalysts in methanation reactions.

4. Conclusions

CO adsorbs dissociately on the surfaces of $Cu_{50}Zr_{50}$ metallic glass and Zr metal, leading to the formation of graphitic and carbidic carbon species. There is a reversal in the population of the two species on the metallic glass surface compared to that on clean Zr.
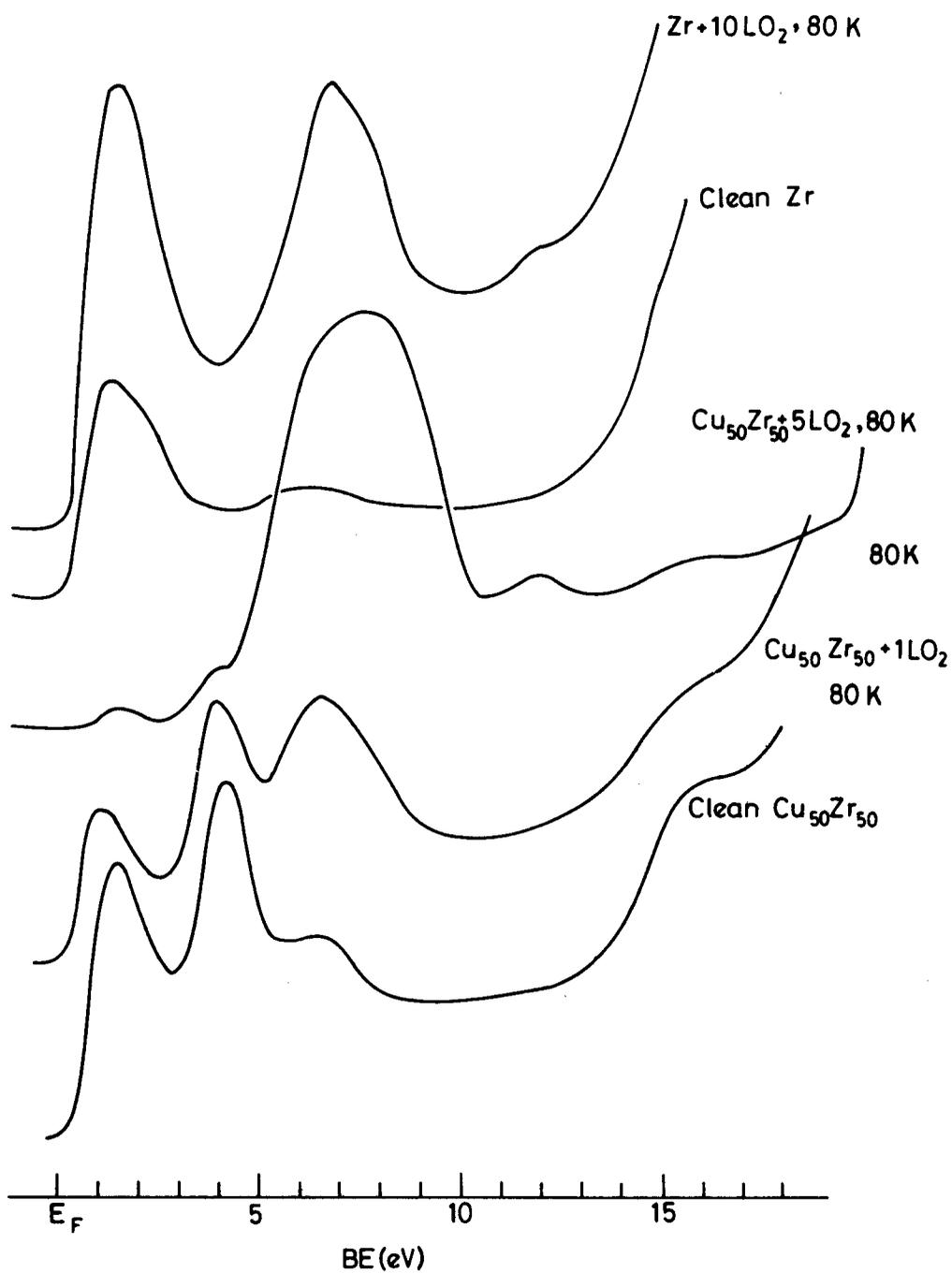
Figure 6. HeII UPS of oxygen adsorption on the $Cu_{50}Zr_{50}$ metallic glass surface and Zr metal surface.

Acknowledgement

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