

# STRUCTURAL AND VIBRATIONAL PROPERTIES OF DEPOSITED Cu OR Zr SURFACE ADLAYERS ON $\text{Cu}_{46}\text{Zr}_{54}$ BULK METALLIC GLASS

Dimitrios G. Papageorgiou<sup>1</sup>, Andrius Ibenskas<sup>2</sup>, Christina E. Lekka<sup>1</sup> and Giorgos A. Evangelakis<sup>2</sup>

<sup>1</sup>Department of Materials Science and Engineering, University of Ioannina, Ioannina 45110, Greece

<sup>2</sup>Department of Physics, University of Ioannina, Ioannina 45110, Greece

Received: March 29, 2008

**Abstract.** The structural and vibrational properties of Cu or Zr adlayers on  $\text{Cu}_{46}\text{Zr}_{54}$  bulk metallic glass (BMG) were studied by means of Molecular Dynamics simulations based on a semi-empirical potential model in analogy to the Tight Binding scheme in the second moment approximation. We found that upon Zr deposition crystalline adlayers are formed, while mixed nearly crystalline terminal composition is found in the Cu deposition case. In addition, we found that at the very early stages of the depositions atomic rearrangement takes place at the interfaces very quickly, while the atomic diffusion within the adlayers is rather limited for temperatures up to 500K. Above this temperature some diffusive activity sets in the Zr adlayers, while the mixed adlayers are subject to reconstruction that is driven from Cu diffusion resulting in an amorphous face. Moreover, we found that the mean square displacements of the Zr adlayer increase linearly with temperature up to 600K, while for the Cu adlayer the same quantity at the higher temperature studied exhibits strong anharmonic increase.

## 1. INTRODUCTION

Bulk Metallic Glasses exhibit high glass forming ability, very good stability with respect to crystallization, good processing capability and a lot of technologically interesting properties, among which we distinguish their exceptional mechanical properties, the wear and thermal resistance, the anticorrosion ability, etc. [1-11]. These properties make the BMGs potential candidates for interesting applications and have acquired great deal of scientific and technological attention the last two decades [12-16]. However, the majority of the studies focus on the bulk properties of the BMGs, while investigations concerning their surface behaviour is limited to corrosive resistance [17], biocompatibility [18,19] and to cases that are related to applications dealing with catalysis [20,21]. In addition, to our knowledge

studies on the modifications and/or functionalization of BMG surfaces are rather scarce and limited to a ZrCu case for which surface alterations were found under Ar ion irradiation [22], revealing Zr enrichment of the outermost layers, while surface structural information upon atomic depositions are lacking.

The aim of the present work is the study of the  $\text{Cu}_{46}\text{Zr}_{54}$  surface modifications occurring upon Zr or Cu deposition. Our choice was dictated from the fact that there are a lot data for this system and also from the availability of a reliable interatomic potential model.

## 2. COMPUTATIONAL DETAILS

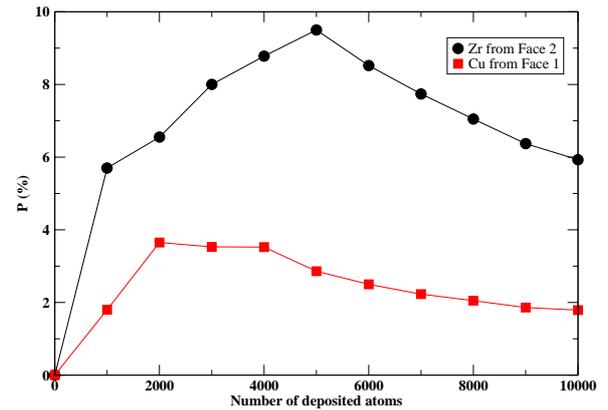
We used a semi-empirical model in analogy to the Tight Binding Scheme in the Second Moment

Corresponding author: Giorgos A. Evangelakis, gevagel@cc.uoi.gr

Approximation for which it was found that it reproduces satisfactorily the glass transition temperature and other properties of the bulk amorphous alloy [23]. The simulation cell we used consisted of 128000 atoms corresponding to the CuZr stoichiometric alloy that were arranged initially in a cubic lattice of B2 structure with periodic boundary conditions. In order to obtain a liquid bulk alloy system we substituted randomly 4% of Cu atoms with Zr and we heated the resulting system to 2000K. The equations of motion were integrated by means of the Verlet's algorithm [24] and a time step of 5fs. Subsequently, we cooled gradually the system down to 300K with a temperature step of 100K performing 20000 integration steps at each temperature in the Isothermal-Isobaric canonical ensemble. The equilibrated simulation box yielded a volume of 2318 nm<sup>3</sup> that was further thermalized at room temperature for 50000 additional micro-canonical integration steps. Subsequently, a slab delimited by two surfaces was created by removing the periodic boundary conditions in one direction and the final system was also equilibrated for 50000 time-steps in the isothermal canonical ensemble. Of course the cooling rate imposed by this procedure is by far greater from what is generally used experimentally; nevertheless, this procedure has been proved to result in a glassy bulk alloy [23], a fact that was of course *a posteriori* verified by the calculated radial distribution functions.

The depositions were done by putting randomly 1000 Zr atoms on one side of the slab (Face 1) and an equal number of Cu particles on the other side (Face 2). After a relaxation of 2000 micro-canonical time-steps another 1000 particles were deposited followed by three more relaxation - depositions of 1000, 2000, and 6000 additional atoms. The obtained four deposition configurations were subsequently equilibrated at various temperatures from 300K to 600K for 100000 time-steps in the micro-canonical ensemble, while 20000 further integration steps were performed and used for the calculations of the various quantities.

Information concerning the structural evolution during the deposition was obtained through the calculation of the percentage of Cu or Zr atoms in the upper four layers of Face 1 or 2 with respect to the number of the deposited Zr or Cu atoms respectively, as a function of the number,  $n$ , of the deposited atoms,  $p(n)$ . We note that this quantity provides a measure of the rate with which the migrating atoms of type A populate the deposited overlayers that are of type B, thus yielding infor-



**Fig. 1.** Number (%) of Cu or Zr atoms on Face 1 or Face 2 with respect to the deposited number of Zr or Cu atoms.

mation on the mass transfer occurring at the interface at the very early stages of the deposition.

In addition, for the quantification of the resulting structures we calculated the time dependence of the Common Neighbour Analysis indices (CNA) [25,26]. According to this method, one counts the number of common neighbours in the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> neighbourhood of all atoms. The three numbers thus obtained, known as CNA indices, can provide evidence for the structure of the system. For instance, the index 421 refers to the FCC structure, the 444 at 42.8% and 666 at 57.2% to BCC, while the 421 and 422 at equal percentages to HCP. Combinations of above indices with other numbers give structural information in presence of surfaces and/or imperfect structures [26]. The mean square displacements and the diffusion coefficients were calculated by means of the Green-Kubo relation of the velocity auto-correlation function [24] and via the following relation:

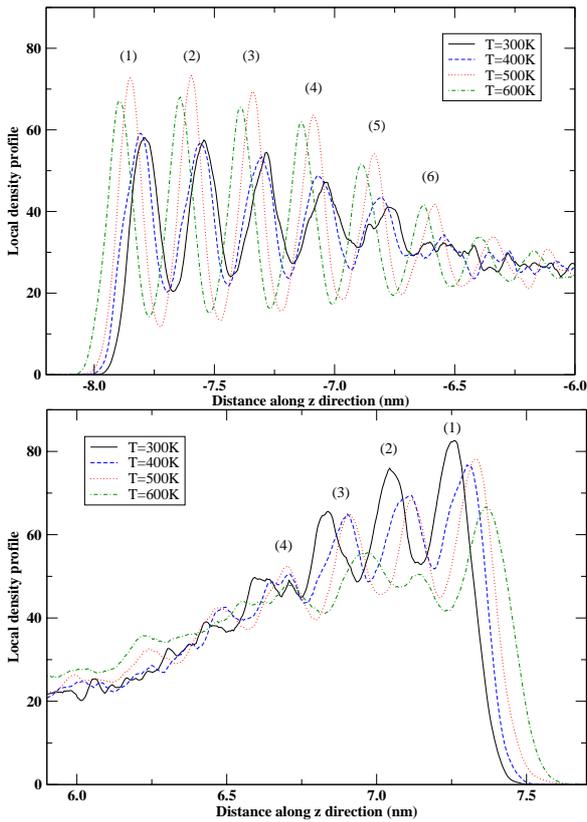
$$\langle \delta r^2(\tau) \rangle = \frac{1}{N} \sum_{i=1}^N \langle |\vec{r}_i(t) - \vec{r}_i(t + \tau)|^2 \rangle, \quad (1)$$

where  $r_i$  stands for the position vector of particle  $i$ .

## 3. RESULTS AND DISCUSSION

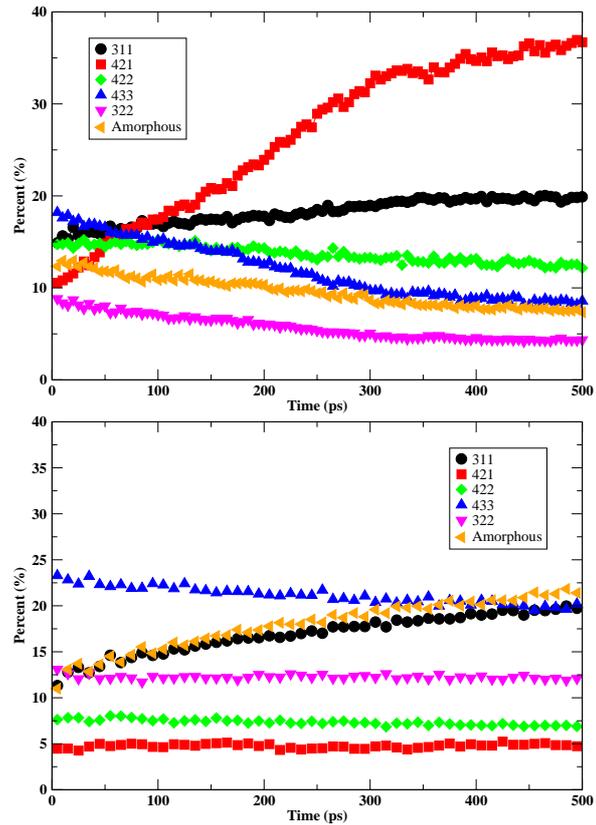
### 3.1. Structuring and Ordering processes

In Fig. 1 we give the  $p(n)$  evolution, for Cu and Zr of the upper four layers of Face 1 (squares) and 2



**Fig. 2.** a) Atomic local density profile of Face 1 after the final deposition of Zr atoms at various temperatures. b) same as in case (a) but for Face 2; note the loss in the layering at  $T=600\text{K}$ .

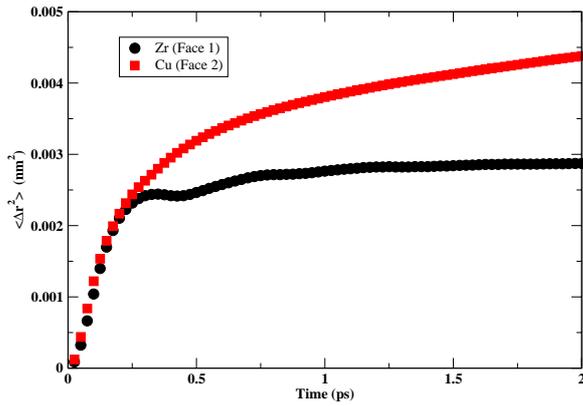
(circles) upon deposition of Zr and Cu respectively. We can see in this picture that in Face 1 the rate evolution of the Cu content of the outer layers upon Zr deposition exhibits a small increase up to 2000 deposited Zr atoms, followed by a decrease just after, reaching very quickly a plateau value of approximately 2%. This result indicates that Zr layering occurred on this surface that has reached a steady state. Indeed, inspection of the local density profile, Fig. 2a, reveals the progressive structuring of this face. On the contrary, on Face 2 the rate evolution in Zr content exhibits a rapid increase upon Cu deposition that is longer than in the previous case, reaching a maximum of almost 10%, before dropping continuously to 6% at the end of the deposition process. This finding indicates that the layering in this case is less pronounced and also that mixing is present. The effect can be clearly seen in the local density profile of this face, Fig. 2b.



**Fig. 3.** a) Percentage of the most important indices of Face 1 after the final deposition of Zr atoms at  $T=500\text{K}$ . b) same as (a) but for Face 2.

In order to gain insight in the structuring process happening because of these depositions we performed CNA analysis for both overlayers. The time evolution of the most important CNA indices for the cases of deposition at  $T=500\text{K}$  of 10000 Zr and Cu atoms is shown in Figs. 3a and 3b, respectively. As it can be seen from these figures the processes occurring on Faces 1 and 2 exhibit qualitative differences: in Face 1 we find a significant increase of the 421 index at expense of the 322, 433 and the amorphous indices (considered as the sum of 000, 100, 200, and 300 indices). We interpret this result as a clear indication of formation of polycrystalline closed packed HCP surface structure.

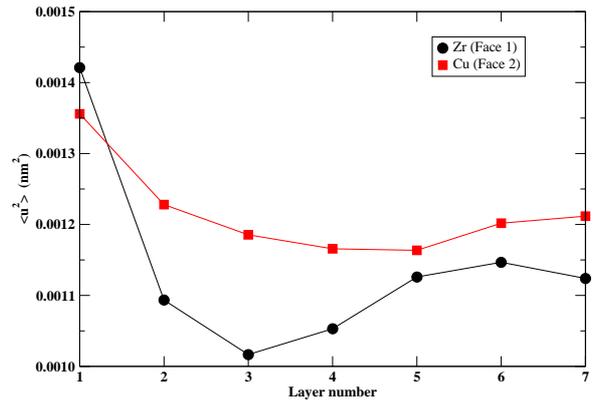
On the contrary, in Face 2 indices 421, 422 and 311 remain almost unchanged, while the amorphous and 433 indices are increased by a factor of two. Combining this result with the conclusions drawn from the composition and the local density profile, Fig. 1 and Fig. 2b, we attribute this behaviour to partial FCC like truncated and mixed ordering in



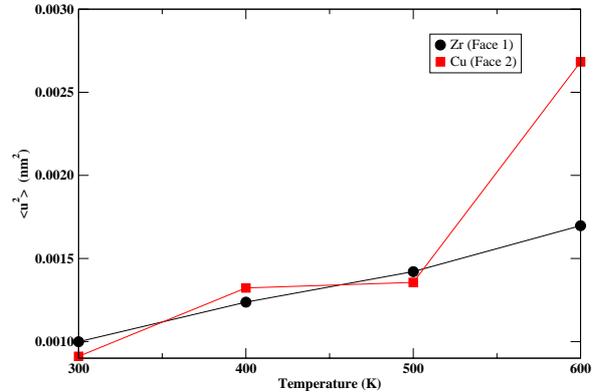
**Fig. 4.** Mean square displacements ( $\langle \delta r^2 \rangle$ ) for Zr atoms on Face 1 and Cu atoms on Face 2 at  $T=500\text{K}$ .

this adlayer. The later is possibly due also to incomplete equilibration within the time scale of our simulations. It is worth noting that the interface between the adlayers and the glassy system are also structurally different. This can be seen from the values of the same indices at  $t=0$ . It turns out that the interface below Face 1 exhibits clear HCP polycrystalline signature (almost equal 421, 422, 311 and 322 indices). The 421 and 422 indices in the interface below Face 2 have rather small values, while the only important index appears to be the 433, a result that indicates partial crystallization and presence of truncated crystallites. We conclude therefore that upon these depositions rearrangements take place very close to the interface with the Zr moving further than Cu atoms, a result that is rather unexpected if we take into account the larger diffusivity of Cu compared to Zr atoms, as given from Hydrogen induced surface segregation studies [27,28]. However, these data refer to chemical reactions occurring at the surfaces and therefore they may not be applicable under the deposition conditions considered in the present work.

For the determination of the diffusivity within the deposited adlayers, we calculated the diffusion coefficients for both Zr and Cu atoms at several temperatures. In Fig. 4 we present the mean square displacements for Zr and Cu adlayer atoms, circles and squares respectively, as calculated via Eq. (1) at  $T=500\text{K}$ . It turns out that even at this relatively high temperature the diffusion coefficients, given by the slope of these curves at the long time tail, or



**Fig. 5.** Mean square displacements ( $\langle \delta r^2 \rangle$ ) of Zr atoms on Face 1 and Cu atoms on Face 2 for the successive atomic layers at  $T=500\text{K}$ . Layer 1 represents the topmost layer.



**Fig. 6.** Mean square displacements of Zr and Cu atoms of the topmost layers of Face 1 and Face 2 as a function of temperature.

by the Green-Kubo formula of the velocity autocorrelation function, are of the order of  $10^{-7} \text{ cm}^2/\text{sec}$ , values that are within the accuracy limits of our simulations. We conclude therefore that as far as there is a concentration gradient that is imposed by the atomic depositions, local atomic rearrangement takes place very fast at the interface region, but the diffusion of any species above the interface and within the deposited overlayer reaches rapidly a steady state of a rather limited diffusivity.

However, at higher temperatures this situation is altered with the Cu and Zr atoms exhibiting diffusion coefficients that, at  $T=600\text{K}$ , are of the order of  $10^{-5} \text{ cm}^2/\text{sec}$  and  $10^{-6} \text{ cm}^2/\text{sec}$  respectively. These values although higher from the diffusivities of the bulk glassy case, are in agreement with the experimental findings according to which in the

ZrCu glassy alloy Cu is more diffusive than Zr, while they are lower from the values corresponding to the adatoms diffusion on the surfaces of the pure elements [29,30]. It appears therefore, that at high temperatures significant interlayer mass transport occurs and affects the picture of the clear structuring of the adlayers.

This issue requires, nevertheless, further investigation in order to reveal the diffusion mechanisms and the dynamics that are involved, a subject that is beyond the scope of the present study.

### 3.2. Vibrational properties

From the calculated mean square displacements we also deduced the vibrational amplitudes ( $\langle u^2 \rangle$ ) of the Zr and Cu atoms of the adlayers 1 and 2 at  $T=500\text{K}$ , Fig.(5). As it would be expected the outermost layers exhibit enhanced  $\langle u^2 \rangle$  for both species, with Zr atoms (circles) showing enhanced vibrational amplitudes compared to the Cu surface atoms (squares). It is worth noticing also that the  $\langle u^2 \rangle$  values for Cu are by an order of magnitude larger than those exhibited by the Cu adatoms on the Cu [29,31] or Au (111) surface [30], while this enhancement of the vibrational amplitudes is even greater in the case of the Zr atoms. In addition, from the same figure it comes out that the  $\langle u^2 \rangle$  values decrease as going in the inner layers, both reaching the value of the glassy alloy,  $0.00117\text{nm}^2$ , after the 5<sup>th</sup> layer. Moreover, from the calculated temperature dependence of this quantity it came out that for the well structured Zr layers the  $\langle u^2 \rangle$  of the topmost layer exhibit a clear linear dependence, while an oscillating character was revealed for the Cu atoms of the topmost layer of Face 2, ending with a strong anharmonic increase at  $T=600\text{K}$ , (Fig. 6). This result, in conjunction with the relatively high diffusivity within the mixed terminations of Face 2 that is found for Cu at this temperature, suggests that the overlayers are subject to reconstruction leading this face to an amorphous state. The effect is also visible in Fig. 2b (dashed-dotted line) by the significant losses of peaks in the atomic local density profile, a result that was also verified by CNA analysis.

### 4. CONCLUDING REMARKS

In this communication we presented Molecular Dynamics simulations results on the structural and vibrational properties of Cu or Zr adlayers on  $\text{Cu}_{46}\text{Zr}_{54}$  bulk metallic glass. We found that upon Zr deposition crystalline adlayers are formed, while

partially crystallized mixed terminal composition is found in the Cu deposition case. In addition, we found that the mean square displacements of the Zr adlayer increase linearly with temperature up to  $600\text{K}$ , while for the Cu adlayer the same quantity at the higher temperature studied exhibits strong anharmonic increase. Moreover, we found that at the very early stages of the depositions atomic rearrangement takes place at the interfaces very quickly, while the atomic diffusion within the adlayers is rather limited at least for temperatures up to  $500\text{K}$ . Above this temperature some diffusive activity sets in the Zr adlayers, while the mixed adlayers are subject to reconstruction that is driven from Cu diffusion resulting in an amorphous face.

### ACKNOWLEDGEMENTS

The present work was supported by the MRTN-CT-2003-504692 project.

### REFERENCES

- [1] K. Lee, K. Euh, S. Lee and N.J. Kim // *J. Alloys and Comp.* **400** (2005) 171.
- [2] K. Asami, C.-L. Qin, T. Zhang and A. Inoue // *Mater. Sci. Eng.* **A375–377** (2004) 235.
- [3] A. Gebert, R.V. Subba Rao, U. Wolff, S. Baunack, J. Eckert and L. Schultz // *Mater. Sci. Eng.* **A375–377** (2004) 280.
- [4] H.B. Yao, Y. Li and A.T.S. Wee // *Electrochimica Acta* **48** (2003) 2641.
- [5] S. Pang, C. Shek, T. Zhang, K. Asami and A. Inoue // *Corros. Sci.* **48** (2005) 625.
- [6] A. Dhawan, S. Roychowdhury, P.K. De and S.K. Sharma // *J. non-Cryst. Solids* **351** (2005) 951.
- [7] A. Inoue, T. Zhang and T. Masumoto // *Mater. Trans. JIM* **30** (1989) 965.
- [8] A. Inoue, H. Kato and T. Masumoto // *Mater. Trans. JIM* **32** (1991) 609.
- [9] A. Peker and W.L. Johnson // *Appl. Phys. Lett.* **63** (1993) 2342.
- [10] A. Inoue // *Acta Mater.* **48** (2000) 279.
- [11] A.R. Yavari // *Nature* **439** (2006) 405.
- [12] A.L. Dreham, A.L. Greer and D. Turnbull // *Appl. Phys. Lett.* **41** (1982) 716.
- [13] A. Inoue, T. Zhang and T. Masumoto // *Mater. Trans. JIM* **31** (1990) 425.
- [14] T. Zhang, A. Inoue and T. Masumoto // **32** (1991) 1005.
- [15] A. Inoue and A. Takeuchi // *Mater. Trans. JIM* **43** (2002) 1892.

- [16] W.H. Wang, C. Dong and C.H. Shek // *Mater. Sci. Eng. R.* **44** (2004) 45.
- [17] S. Hiromoto, A.P. Tsai, M. Sumita and T. Hanawa // *Corr. Sci.* **42** (2000) 2167.
- [18] J.A. Horton and D.E. Parsell // *Mater. Res. Soc. Symp. Proc.* **754** (2003) CC1.5.1.
- [19] S. Hiromoto, K. Asami, A.P. Tsai and T. Hanawa // *Mater. Trans.* **43** (2002) 261.
- [20] T. Takahashi, M. Inoue and T. Kai // *Appl. Catal.* **A218** (2001) 189.
- [21] Y.J. Yoon, K.W. Kim, H.K. Baik, S.W. Jang and S.M Lee // *Thin Solid Films* **350** (1999) 138.
- [22] H.J. Kang, C.H. Kim, N.S. Park, D.J. O'Connor and E. MacDonnald // *Appl. Surf. Sci.* **100/101** (1996) 329.
- [23] G. Duan, D. Xu, Q. Zhang, G. Zhang, T. Cagin, W.L. Johnson and W.A. Goddard III // *Phys. Rev.* **B71** (2005) 224208
- [24] A. Rahman // *Phys. Rev.* **136** (1964) A405.
- [25] J.D. Honeycutt and H.C. Andersen // *J. Phys. Chem.* **91** (1987) 4950.
- [26] A.S. Clarke and H. Jonsson // *Phys. Rev. E* **47** (1993) 3975.
- [27] F. Vanini, M. Erbudak, G. Kostorz and A. Baiker // *Mater. Res. Soc. Symp. Proc.* **111** (1987) 375.
- [28] M. Kilo, M. Hund, G. Sauer, A. Baiker, A. Woan, J. Alloys and Comp. **236** (1996) 137
- [29] G.C. Kallinteris, G.A. Evangelakis and N.I. Papanicolaou // *Surf. Sci.* **369** (1996) 185.
- [30] G.A. Evangelakis, G.C. Kallinteris and N.I. Papanicolaou // *Surf. Sci.* **394** (1997) 185.
- [31] C. Barreteau, F. Raouafi, M.C. Desjonqueres and D. Spanjaard // *Surf. Sci.* **519** (2002) 15.