Local atomic order of a metallic glass made visible by scanning tunneling microscopy

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Abstract

Exploring the atomic level structure in amorphous materials by STM becomes extremely difficult due to the localized electronic states. Here we carried out STM studies on a quasi-low-dimensional film of metallic glass Zr₆₅Cu₂₇.₅Al₇.₅ which is ‘ultrathin’ compared with the localization length and/or the length scale of short range order. The local electronic structure must appear more inherent, having states at \( E_f \) available for tip-sample tunneling current. To enhance imaging contrasts between long-range and short-range orders, the highly oriented pyrolytic graphite was chosen as substrate, so that the structural heterogeneity arising from competition between the glass former ability and the epitaxy can be ascertained. A chemical order predicted for this system was observed in atomic ordered regimes (1–2 monolayers), accompanied with a superstructure with the period Zr–Cu(Al)–Zr along three hexagonal axes. The result implies a chemical short range order in disordered regimes, where polyhedral clusters are dominant with the solute atom Cu(Al) in the center. An attempt for the structural modelling was made based on high resolution STM images, giving icosahedral order on the surface and different Voronoi clusters in 3D space.

Keywords: local atomic order, amorphous materials, metallic glasses, scanning tunneling microscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Dissimilar to crystals, amorphous materials possess a short range order (SRO), but no long-range structural correlation [1]. Conventional experiments, such as widely used x-ray/neutron diffractions [2–5], deliver usually statistical data about the structure, but no details about local atomic configurations. Computer simulation based on several models [6–10] could provide otherwise an alternative in solving and studying the amorphous structures and helps to construct and visualize a 3D structure. However, one must always keep in mind a large disparity between the computer world and the real world in terms of the time and spatial scales [1]. A direct observation of local atomic order in a metallic glass was achieved recently in a milestone work made by Hirata et al. [11], using nanobeam electron diffraction (NBED) technique with a beam size and a sample thickness both down to an order of magnitude corresponding to the length scale of SRO.

In present work, we report atomic images measured by STM for an ultrathin film Zr₆₅Cu₂₇.₅Al₇.₅ deposited on a highly oriented pyrolytic graphite (HOPG) substrate. As well known, STM relies on tunneling current between the tip and sample, which can be used to sense the topography of the surface. The correspondent research has mainly focused on ordered systems, which reveal a periodic potential according to Bloch’s modes (see figure 1(a)) and a number of unfilled electronic states at \( E_f \). Metallic glasses possess dissimilarly a ‘randomly fluctuated’ potential and the electronic state is localized due to the structural disorder, i.e. Anderson localization [12] as schematically illustrated in figure 1(b), where the wave function of electrons is damping down exponentially with \( r \) and approaching to zero at \( r = \zeta \). Here \( \zeta \) is denoted as the localization length, which is comparable to the scale of SRO. The electronic localization may give rise to a broadening state with...
Figure 1. Schemes of periodic wave function of crystals (a) and Anderson localization in amorphous materials (b) with \( \zeta \) denoted as the localization length.

Taking the SRO nature of the amorphous materials into account, however, the local electronic structure must appear somehow more inherent regarding Anderson transition [16], if the local potential fluctuation within the SRO is not too strong. The feature must be detectable by the atomically sharp probe of STM, as soon as the sample gets sufficiently thin comparable to the SRO scale (quasi-low-dimensional with respect to the electron state localization length). The scenario is then similar to the NBED experiment mentioned above. Furthermore, as a prerequisite condition for STM experiments, an atomic highly ordered surface from the substrate is necessary, which creates imaging contrasts between long-range and short-range orders and has no chemical reaction to the film. The HOPG version of carbon is an ideal candidate and it is also often studied by STM. We chose the metallic glass \( \text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5} \) as the disordered system due to its good glass former ability (GFA). By a low cooling rate it can cast into a fully glassy sample with a diameter \( \geq 1 \text{ mm} \), conventionally called bulk metallic glass (BMG) [17]. The BMGs are strong and moldable, thus being of high technical importance [18, 19].

2. Experimental details

Ultrathin film of \( \text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5} \) was prepared onto HOPG \((0.5 \times 0.5 \text{ cm}^2)\) by pulse dc-magnetron sputtering. The HOPG surface was cleaned by tape technique. The base pressure of the chamber and the sputtering pressure of Ar gas are about \( 2 \times 10^{-7} \text{ and } 0.5 \times 10^{-3} \text{ mbar} \), respectively. 1 pulse of duration 1s was used and the ultrathin film has a mean thickness less than 1 nm, as estimated from the height histogram of relevant STM height images (see figure 4(c)) or from data measured for a calibration film (usually 5–100 nm) by small angle x-ray scattering. The substrate temperature is 300 K and a contamination from substrate atoms (carbon) can be here eliminated. The target used was commercially purchased with a purity of 99.9%. It is already at a chemically stoichiometric equilibrium state after an intensive usage for studies of ultrastable metallic glass [20]. Standard STM measurements on the nanoscale operating in constant-current and constant-height modes were carried out \( \text{ex situ} \) using a commercial instrument Nanoscope IV from Veeco \((510 \times 510 \text{ image pixels})\) with a tip-sample bias of 10 mV and a current set point of 1nA. A high scan rate of 60 Hz was used to minimize the image capture time (here about 8 s) and possible image distortions arising from thermal drift or hysteric behavior of the piezoelectric element. The STM experiment was performed straightaway after film deposition and finished in a few minutes. For this short period, we noticed that the effect of surface oxidation (mainly zirconia) in air is not pronounced. It is well known that a high electric resistant oxide may deteriorate the STM images. This could be seen (not shown here) only for the film exposed in air for a relatively long time (12 h more). To check the quality of the STM tip used, we measured also atomic images (honeycomb) of HOPG before (see figure 2(a)), whose lattice parameter \((0.142/0.246 \text{nm})\) is well known. The length scale of the scanner could be calibrated thereby.

Several evaluations, such as power spectral density (PSD), which represents periodically or randomly distributed surface features as a function of the spatial wavelength, fast Fourier transforms (FFT), section profile as well as depth/height and bearing analysis were performed for measured STM images by means of a special software [21], where the bearing analysis reveals how much of surface or atoms standing above or below a given depth of images. The operation of the bearing step by step yields additional information about atom positions layer by layer and thus the atomic packing in 3D space (details see figure 6). The structural units were constructed then by interconnecting the nearest neighbors around a central atom according to the Voronoi tessellation method [22], which divides the 3D space into cells by drawing planes bisecting the joining lines between the central atom and all its neighbors. The local structures and the coordination numbers \( N_i \) of the nearest neighbors were identified with the help of Voronoi indexes \( \{n_3, n_4, n_5, n_6\} \), where \( n_i \) is denoted as the number of \( i \)-edged faces on the Voronoi polyhedron (subscripts \( i \); 3 = triangles, 4 = quadrangles, 5 = pentagons and 6 = hexagons). The sum of the index \( \sum n_i = N_c \).

3. Results and discussion

3.1. STM current images and chemical ordering

Figure 2(b) is a STM current image \((10 \times 10 \text{nm}^2)\) measured for the ultrathin film \( \text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5} \) deposited on HOPG, showing atomic level structures consisting of atomic ordered and disordered regimes. The structural heterogeneity (including surface corrugation) arises likely from the...
competition between the GFA and the epitaxy mentioned. In ordered regimes the atomic arrangement exhibits a six-fold symmetry similar to the honeycomb structure of HOPG given in figure 2(a). However, the interatomic spacing measured along three hexagonal axes is about 0.287 nm in average. It is larger than that (0.246 nm) of the HOPG, but close to the mean atomic size $2r$ = 0.297 nm of the sample, calculated from $\sum 2r_i c_i$ where $c_i$ is denoted as the concentration and $r_i$ as Goldschmidt atomic radii of Zr(0.159 nm), Cu(0.128 nm) and Al(0.143 nm). Moreover, the current scale used for figure 2(b) is maximal 4 nA, much larger than 0.5 nA for figure 2(a), reflecting the fact that the metallic atoms of Zr and Cu(Al) possess more unfilled electronic states at $E_f$ than the later transition metal Cu [13], the surrounding atoms reveal a higher tunneling current than the center atoms. For this reason, we argue that the center atoms are the solute Cu(Al) and the surrounding atoms the solvent Zr. In fact, earlier ultraviolet photoelectron spectroscopy (UPS) investigations on Zr$_{1-x}$Cu$_x$ systems [25, 26] could point out that the d-band of Zr and Cu shifts oppositely to the low and high energy direction respectively, and the electronic structure at $E_f$ is accordingly dominant by the d-band of Zr. The result observed here is an indication of the chemical order associated with the strong interaction between Zr and Cu due to a large negative heat of mixing [1]. For the composition used, the 35% solute atoms appear seldom in pairs, but surrounded by 65% solvent atoms, as is confirmed below by bearing analysis (see figure 3(a)). The chemical order is expected to extend into the disordered regimes due to chemical short-range order (CSRO) [27].

Figure 3(a) illustrates another STM current image (5 $\times$ 5 nm$^2$) of the sample, showing a box selected for bearing analysis. The box is chosen in the ordered regime and it contains 120 atoms in total. Among them about 78 atoms change in ‘color’ (red) upon bearing at a certain depth (here 0.2 nA). These atoms all sit down at corners of the hexagon, while other 42 atoms, which remain unchanged in color, are caged at the center of the hexagon. The ratio of the atom number was found to be 42/120 = 0.35, and 42/120 = 0.35, respectively, just equal to the concentration of Zr and Cu(Al) atoms. Individual atomic size of Zr and Cu(Al) for the ordered phase can be determined thereby. They are equal to $0.295$ nm and $0.264$ nm respectively, and slightly smaller than the Goldschmidt atomic radii as discussed before.

To interpret the atomic distribution, 1D and 2D PSDs were calculated for the images given in figure 2(b). The results are plotted as function of the spatial wavelength in figure 2(c), displaying additionally a broad maximum, which is similar to the first maximum of radial distribution functions (RDF) measured for metallic glasses by conventional x-ray/neutron diffractions [2–5]. The broad maximum is centered at around 0.29 nm in line with $2\pi$ given above.

The chemical ordering is already recognizable in figure 2(b) at several hexagons marked by dashed-line boxes, where a center atom is caged by other 6 atoms. Since the early transition metal Zr possesses more unfilled electronic states at $E_f$ than the later transition metal Cu [13], the surrounding atoms reveal a higher tunneling current than the center atoms. For this reason, we argue that the center atoms are the solute Cu(Al) and the surrounding atoms the solvent Zr. In fact, earlier ultraviolet photoelectron spectroscopy (UPS) investigations on Zr$_{1-x}$Cu$_x$ systems [25, 26] could point out that the d-band of Zr and Cu shifts oppositely to the low and high energy direction respectively, and the electronic structure at $E_f$ is accordingly dominant by the d-band of Zr. The result observed here is an indication of the chemical order associated with the strong interaction between Zr and Cu due to a large negative heat of mixing [1]. For the composition used, the 35% solute atoms appear seldom in pairs, but surrounded by 65% solvent atoms, as is confirmed below by bearing analysis (see figure 3(a)). The chemical order is expected to extend into the disordered regimes due to chemical short-range order (CSRO) [27].

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The chemical modulation observed behaves as atomic chains along three hexagonal axes with a common periodicity of Zr–Cu(Al)–Zr. A superstructure appears accordingly in relevant STM images. Figure 3(b) reveals a FFT pattern obtained from figure 3(a). It consists of three structural components; (i) Bragg lattice indicated by six circles (small) with a long distance in the reciprocal spacing, (ii) superstructure represented by six circles (large) with a short reciprocal spacing and (iii) medium-range structure of disordered regimes characterized by scattered spots near the FFT pattern center. The corresponding images extracted by Fourier-filter were shown in figures 3(c)–(e). With respect to the Bragg lattice (figure 3(c)) the superlattice (figure 3(d)) shows a double interatomic distance with an orientation rotated by about 30 degrees. The figure 3(e) gives structural features of MRO, including lateral dimension (within 1 nm) and distribution of atomic clusters. Our earlier STM studies [14] on Zr65Cu27.5Al7.5 films (∼5 nm) deposited on silicon substrates showed images similar to figure 3(e).

3.2. STM height images

Figure 4(a) gives a height image (5 × 5 nm²) of the sample, showing atomic-level topography of the surface, though the spatial solution is lower than the related current images. The chemical modulation, which is visible in current images, becomes here insignificant due to the exponential relation between tunneling current and tip height. The relevant height histogram was calculated and plotted in figure 4(c), showing nearly a Gaussian distribution with a maximum at about 0.6 nm and a standard deviation of about ±0.2 nm. The height value at the maximum can be approximately recognized as the average thickness of the selected scan area of the film. The corrugation contains actually several atomic clusters with local topological

![Figure 3](image-url)  
(a) STM current image (5 × 5 nm²) measured for ultrathin film Zr65Cu27.5Al7.5 with a bearing box (inset) and FFT pattern (b) as well as Fourier-filtered images of Bragg lattice (c), superstructure (d) and MRO of disordered regimes (e).

![Figure 4](image-url)  
(a) STM height image (5 × 5 nm²) measured for ultrathin film Zr65Cu27.5Al7.5, (b) section profile along the dashed-line given in (a), including a scheme of possible atomic packing, (c) the height histogram, showing a maximum near 0.6 nm, which can be used to estimate the mean thickness of the selected scan area of the film.
ordering. Figure 4(b) shows the section profile extracted along the dashed-line given in figure 4(a) across the corrugation regime. The size of clusters can be estimated thereby. It is about 5–6 atoms in diameter and 3–4 atoms in height, approximately as large as 2–3 polyhedral units. Additionally, as shown in figure 4(b), the separation between two red triangles amounts to 2.91 nm. In between there is space for 10 atoms packed on the corrugated surface. The lateral interatomic spacing is then 0.291 nm in average. The value is the same as observed by PSD analysis (see figure 2(c)).

The atomic packing on the surface can be easily constructed along the section profile. Below the surface it can be only estimated according to the highest packing efficiency, like Bernal’s tetrahedron or octahedron structural units [28]. The atomic species and neighborhoods are schematically demonstrated here according to the concentration of the sample and the chemical ordering observed (see figure 3).

The relationship between the two kinds of STM images on interesting regimes was studied. The result (not shown here) indicates that the surface electronic structure and the surface topography for the ordered (atomically flat) regime are better correlated than those for disordered (corrugated) regime. Likely due to the exponential relation between the tunneling current and the tip height, the correlation of the two kinds of images is valid only for the atomically flat surface.

3.3. Fivefold topology
As it is known, STM is a very surface sensitive technique. It senses the local electronic structure and provides information about the atomic arrangement on the surface only. Nevertheless, the construction of 3D structure is here in principle feasible using additional information. One must keep in mind the size of different polyhedra maximal 2–3 atoms in
height and wide due to the ultrathin film. They are lying down at the film surface with atomic local environments similar to those of crystalline cells. 3D structural units can be constructed if one gets information about atomic packing from topmost atoms down to a depth of about 2–3 atoms. This is feasible based on high resolution STM images either by a series section analysis given in figure 4(b) or by a multistep bearing analysis shown in figure 6.

The first attempt was made however using a current image (10 × 10 nm²) given in figure 5(a). It contains a huge disordered regime in a pentagonal form with a side length of about 2 nm. Based on the observation mentioned before, the high peaks assumably stem from the topmost atoms, namely the solvent Zr. Interconnecting the local bond around we found a number of fivefold local environments, as can be followed in figure 4(b). The fivefold topology belongs to the so-called icosahedral order, which is thought of as a common structural feature for liquid and metallic glasses. Beneath the fivefold bond there should be a solute atom Cu or Al due to the chemical order observed, which results in preferential local bonds of Zr–Cu(Al)–Zr. The addition of a few percent Al is shown to increase the relevant polyhedra around both Cu and Al and thus enhances overall the fivefold topology and icosahedral order [1]. Actually, the picture given in figure 5(b) can be designated as the icosahedral clusters exposed to the surface. The interconnection and distribution of these clusters give the information about MRO.

### 3.4. Construction of polyhedra in 3D space

Furthermore, we tried to construct polyhedra in 3D space by multistep bearing analysis [21] from height images. The step used is a depth nearly equal to the mean atomic radius \( r \) (0.143 nm). The operation provides thus useful information about atomic packing from the topmost extended into the film at a certain depth (here about 2–3 atoms). More details can be followed in figure 6. At the bearing depth \( r \), for example, 3 topmost atoms change in color ‘red’ (figure 6(b)), at the depth 2\( r \) other 7 atoms (figure 6(c)) corresponding to the nearest neighbors of the topmost atoms, at 3\( r \) then 20 atoms (figure 6(d)) and so on. Taking the highest packing efficiency into account, the positions of atoms from layer to layer can be determined in this way. Using atoms labelled here with \( a, b, c, \ldots \), a Voronoi cluster \( \{0,2,8,1\} \) in 3D space can be established (see figure 7(b)). Different 3D polyhedral units were found out thereby. Several of them are depicted in figures 7(a) and (b). They can be indexed by Voronoi indexes \([1, 22, 29]\) \( \{0,3,8,2\} \), \( \{0,0,12,0\} \) and \( \{0,2,8,2\} \) with coordination number \( N_C = 13 \) and \( N_C = 9 \). In addition, in terms of the heterogeneity in local atom density and local elastic modulus measured for metallic glasses \([30, 31]\), the \( N_C \) varying from 11 to 13 is reasonable. Otherwise, lower surface packing efficiency may decrease the coordination number, such as \( N_C = 9 \) and give rise to a high density of ‘free volume’ at the surface. For instance, a surface ‘vacancy’ (white) was used for frustration of the cluster \( \{0, 2, 8, 2\} \) (right upper in figure 7(a)).

### 4. Conclusion

In summary, by means of STM we could investigate atomic level structure of an ultrathin film Zr_{65}Cu_{27.5}Al_{7.5}. The nature of local atomic order plays here an important role. It allows STM distinguish local atoms of metallic glasses, as soon as the film is sufficiently thin close to the length scale of SRO (≈localization length) and the local electronic structure appears to be expanded (inherent), having states at \( E_f \) available for tip-sample tunneling current. The atomic highly ordered substrate HOPG serves imaging contrast between the long range period and the SRO of the atomic arrangement, so that the structural heterogeneity, arising from the competition between the good GFA and the epitaxial growth, is visible. We observed therefore an ordered phase of 1–2 monolayers with the chemical order predicted for this system. It gives rise to a superstructure with a period of Zr–Cu(Al)–Zr along three hexagonal axes. Accordingly, it is reasonable to believe CSRO exists in the disordered phase, where the polyhedral clusters are dominant with the solute atom in center. The icosahedral order is directly visible in relevant current images. Different Voronoi cells in 3D space could be constructed from height images so far with the help of bearing analysis.
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