On the use of atomic force microscopy for structural mapping of metallic-glass thin films

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ABSTRACT

In this article, we discuss the recent use of the high-resolution dynamic atomic force microscopy (DAFM) in mapping the nano-scale dynamical structural heterogeneity in thin film metallic-glasses (TFMGs). Our focus is laid on the major factors which can influence the structural contrast in the DAFM images, such as tip radius, free-amplitude, set-point amplitude and surface roughness. Finally, through a comparative study of different TFMGs and single-crystal silicon, we demonstrate that the DAFM technique is effective in distinguishing different nanostructures through their energy dissipation spectra.

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1. Introduction

Unlike crystalline metals with a periodic atomic structure, metallic glasses (MGs) possess an amorphous structure lack of any long-range translational symmetry. Despite the amorphous 'maze' often shown on an electron microscopy image, local 'motifs' of atomic packing, such as the icosahedral and crystal-like packing [1–4], can still be identified from atomistic simulations or electron microscopy. While these static structural features, often known as the short- or medium-range order (SRO or MRO), are commonly referred to as the structural building blocks of MGs in the literature [1–4], however, amorphous structures are not meant to be 'static'. Under a thermal or mechanical loading, they can be relaxed or rejuvenated, transitioning from one glassy configuration to another along the potential energy landscape (PEL) [5]. According to the recent simulations [6], at the onset of yielding, these events of structural rearrangements can span a spatial dimension of several orders of magnitude larger than the size limit (1–3 nm) of SRO or MRO [2,3]. This behavior implies that, in order to gain a holistic structural understanding of MGs, one must turn to the dynamic aspect of amorphous structure. In principle, it is not only the atomic bonding strength but also the relaxation spectrum of the amorphous structure that gives rise to the different properties of MGs [7]; therefore, it is worthwhile to characterize their dynamic structural heterogeneities in one way or another [5,8–11].

In principle, the amorphous structure of MGs can be depicted as a nano-scale composite, consisting of loose- and dense-packing atoms (Fig. 1) [4]. When perturbed by an external agent, the dense-packing atoms respond elastically; whereas the loose-packing ones respond inelastically, of which the behavior resembles that of 'residual' supercooled liquids trapped within an elastic 'matrix' [5]. Therefore, as a reflection of the underlying structural heterogeneity, the MGs as a whole deform in an anelastic fashion.

Recently, several experimental techniques have been devised or employed to reveal anelasticity in MGs, including the cyclic microcompression by Ye et al. [5], the X-ray diffraction from deformed samples by Dmowski et al. [11], the high-rate nano-indentation by Yang et al. [8], and the dynamic atomic force microscopy (DAFM) by Liu et al. [10] and Yang et al. [9]. In those experiments, the detected anelastic deformation spans a wide range of length scales (1 nm–1 mm) [5,8–11], which suggests that, although anelasticity originates from the sites with a local
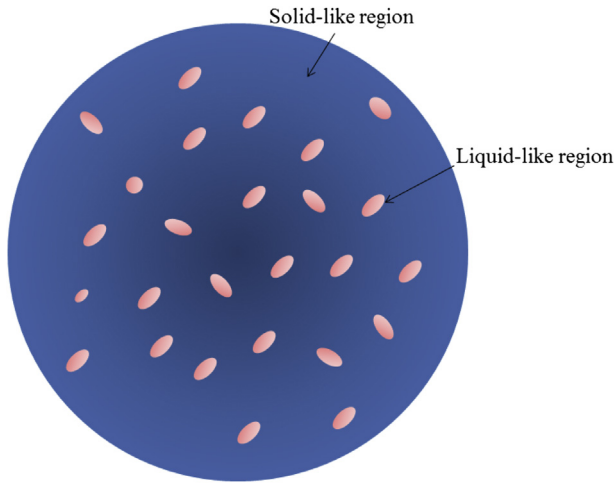
Fig. 1. The schematics of the amorphous structure of MGs.

structural heterogeneity, however, these sites are distributed homogenously in the MG. Consequently, one can observe anelasticity at different length scales once these local sites become activated, as seen in the molecular dynamics (MD) simulations recently performed by Fujita et al. [12]. Among the above experimental techniques, the DAFM method draws much attention because its spatial resolving capability provides a feasible means to map out the whole amorphous structure on a 2-D plane [9,10]. Nevertheless, its use is limited only to thin film metallic-glasses (TFMGs) at this moment due to a stringent surface requirement, which will be discussed in the later text.

2. Theoretical analysis and experimental set-up

2.1. DAFM and nano-scale energy dissipation

Before the discussions of our experiments, we would like to have a brief overview of the DAFM method and the associated energy dissipation mechanisms at the nano-scale. In practice, there are a number of dynamic modes available for operating an AFM. However, our discussion is herein limited to the amplitude-modulation (AM) AFM, also known as the tapping-mode AFM in the literature [13]. Under this dynamic mode, a vibrating AFM tip is engaged with a sample surface at a pre-defined set-point amplitude and vibration frequency. Conceptually, this type of dynamic engagement is equivalent to 'feeding' the sample surface with the same amount of mechanical energies. However, the energy being actually dissipated varies with the site-specific material structure and some other factors, such as surface capillary forces and roughness [9,13–16].

Regardless of the nano-scale energy dissipation mechanisms, the energy dissipated per cycle, E_{dis}, can be expressed as [15]:

$$E_{dis} = \frac{\pi k A_{sp} A_0}{Q} \left[\sin\left(\frac{\pi}{2} - \Delta\varphi\right) - \frac{A_{sp}}{A_0} \frac{\omega}{\omega_0} \right] \quad (1)$$

where k is the spring constant of the AFM cantilever; A_{sp} and A_0 denote, respectively, the set-point and free amplitude; Q is the quality factor; $\Delta\varphi$ is the phase shift measured by the DAFM; and ω and ω_0 represent the respective driving and resonant frequency. Here, it should be noted that, for a high Q value (>200), the quality factor (Q) can be simply calculated as the ratio of the peak frequency ω_0 to the width-at-half-maximum γ of the peak. Meanwhile, the time-average elastic force (F_{ts}) exerted on the sample surface can be also derived, which is $F_{ts} = F_0/2\cos(\pi/2 - \Delta\varphi)$, where $F_0 = kA_0/Q$ [13]. These equations constitute the basic nano-mechanics 'toolkit' for the structural characterization with DAFM.

In 2006, Garcia et al. [17] provides a convenient way to identify the mechanisms of nano-scale energy dissipation in the DAFM. In their work, three different dissipation mechanisms are studied, including the energy dissipation due to long-range surface attraction, surface energy hysteresis and sample viscoelasticity (or anelasticity for metals). In practice, the three mechanisms can be keyed to the three distinctive curves of $\delta E_{dis}/\delta(A_{sp}/A_0)$ versus A_{sp}/A_0, respectively, as shown in Fig. 2a–f. For the case of TFMGs, Liu
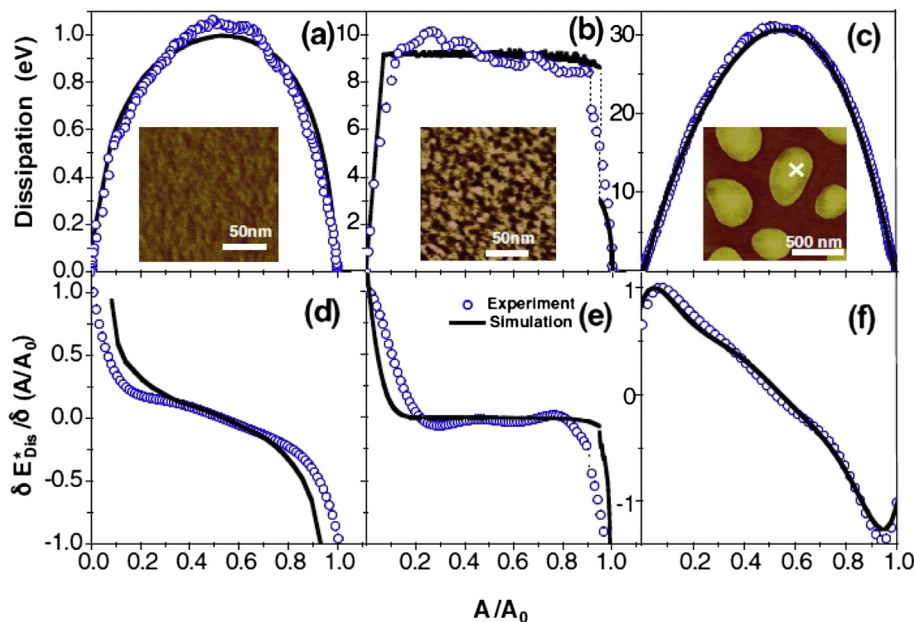

Fig. 2. (a)–(c) The measured and simulated dynamic dissipation curves E_{dis} as a function of the amplitude ratio A/A_0 and (d)-(f) the corresponding derivatives. Note that (a) and (d) are obtained on a silicon surface with $A_0 = 6.6$ nm and $k = 2$N/m, (b) and (e) on a silicon with $A_0 = 32.5$ nm and $k = 2$N/m, and (c) and (f) on a PS region in the blend of a PS/PB polymer with $A_0 = 15$ nm. Note that the images are taken from Ref. [17].