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Five-fold Symmetry in Au-Si Metallic Glass

Chang-Chun He,[a,b] Shao-Gang Xu,[a] and Shao-Bin Qiu,[b] Chao He,[a] Yu-Jun Zhao,[b] Xiao-Bao Yang,[b†] Hu Xu[a,c,‡]

1 Computational Methods

Based on density functional theory, first-principles calculations were performed with the Vienna *ab intio* simulation package (VASP)[1,2] to describe the stability of given structures. The exchange-correlation functional is treated through the Perdew-Burke-Ernzerhof (PBE) in the framework of generalized gradient approximation (GGA)[3]. The kinetic energy cutoff of the plane wave was 350 eV, and the energy convergence criterion was chosen as 10^{-5} eV. The atomic positions and lattice parameters were fully optimized until the forces were less than 0.02 eV/Å for all atoms.

2 Rapid cooling simulations in Au-Si metallic glass

To extract the inherent local structures of $Au_{82}Si_{18}$ metallic glass, the initial configuration with 1000 atoms was constructed based on the thermal-equilibrated bulk Au system, where a certain number of Au atoms were randomly replaced with Si atoms. Each configuration is fully relaxed at T = 2000 K for 10 ps to obtain the initial liquid $Au_{82}Si_{18}$ alloy for the preparation of rapid cooling processes under *NPT* ensemble[4]. Then the large cooling rate, 1×10^{-11} K/s, was used to explore the metastable undercooled structures, where the simulation temperature was quickly reduced to 300 K from 2000 K. To avoid the systematic error, 100 configurations were used to produce structural information, for instance, the averaged coordinate numbers and the partial pair-correlation functions.

a Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China; E-mail: xuh@sustech.edu.cn

b Department of Physics, South China University of Technology, Guangzhou 510640, China; E-email: scxbyang@scut.edu.cn

b Shenzhen Key Laboratory of Advanced Quantum Functional Materials and Devices and Department of Physics, Southern University of Science and Technology, China

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3 Formation energy calculations

For the bulk case, the formation energy for Au-Si is defined by

$$E_{\text{form}} = \frac{E_{\text{total}} - n_{\text{Au}}E_{\text{Au}} - n_{\text{Si}}E_{\text{Si}}}{n_{\text{Au}} + n_{\text{Si}}} \quad (1)$$

where E_{Au} and E_{Si} are the energies per atom in the Au and diamond Si bulk structures. For the surface structure case, the substrate was constructed by a six-atom-thick slab model and the atomic position of the lowest Au layer were fixed during the full relaxation. A vacuum space of about 15 Å was used to avoid the interactions of neighboring images. When Si atoms deposit on substrate, there are various possible surface structures, such as an isolated Si atom, Si clusters, Si monolayer, and Au-Si surface alloy. The formation energy is defined as:

$$E_{\text{form}} = \frac{E_{\text{total}} - E_{\text{sub}} - n_{\text{Au}}E_{\text{Au}} - n_{\text{Si}}E_{\text{Si}}}{n_{\text{Si}}} \quad (2)$$

where E_{total} is the total energy of the whole system, E_{sub} is the energy of the substrate, n_{Au} and n_{Si} are the numbers of Au (if any) and Si in the topmost layer, E_{Au} and E_{Si} are the energies per atom in the Au and Si bulk.

4 Formation energy of Au-Si monolayers

High-throughput first-principles calculations have been performed to determine the possible surface structure on Au(111) substrate. As shown in Fig. S1, our results point out that Au-Si monolayers with Au_5Si pyramid are rather stable compared with those monolayers without Au_5Si pyramid, where the formation energies of Au-Si monolayers with Au5Si pyramids are apparently lower. The most stable Au-Si monolayer on the Au(111) substrate is depicted in the right inset of Fig. S1, which is assembled by the Au_5Si pyramids.
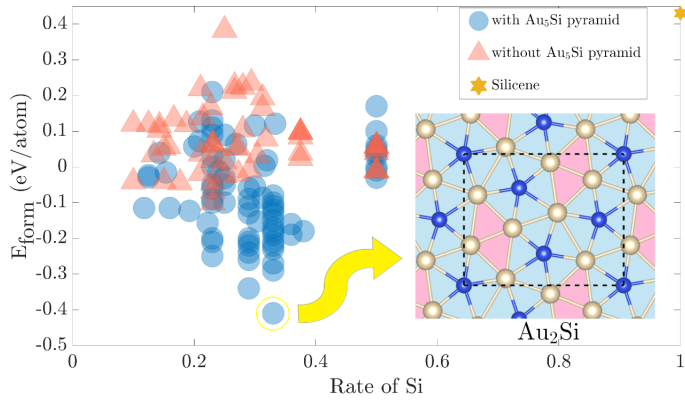
Fig. S1 The formation energy of a few Au-Si monolayers on the Au(111) substrate.

Fig. S3 The formation energy of the AuSi monolayers, where the blue and red points indicate those monolayers without and with Au5Si pyramid, respectively.

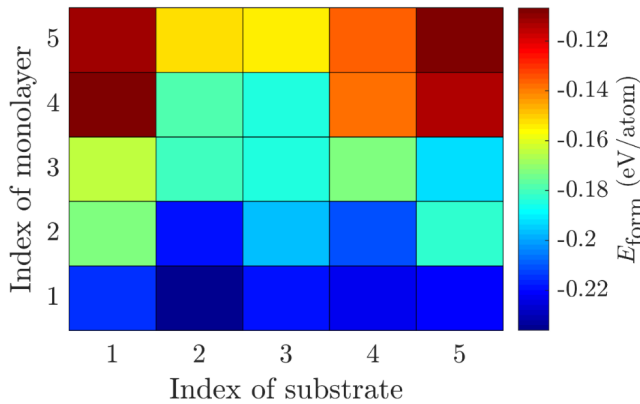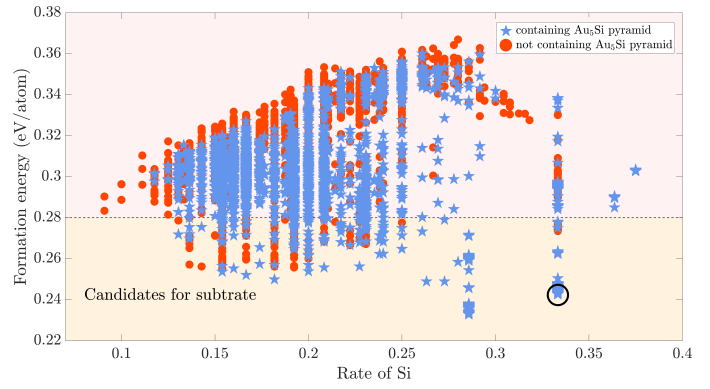## 5 Formation energy of Au-Si monolayers on the surface of Au-Si metallic glass

Fig. S2 The formation energy of a few Au-Si monolayers on the surface of $Au_{82}Si_{18}$ metallic glass structures.

The top five Au-Si monolayers with the lowest formation energies on Au(111) are selected to construct the surface structures of liquid Au-Si alloy, where the first and last layers were substituted by the stable Au-Si surface structures. The formation energy is defined as:

$$E_{\text{form}} = \frac{E_{\text{total}} - E_{\text{sub}} - n_{\text{Au}}E_{\text{Au}} - n_{\text{Si}}E_{\text{Si}}}{n_{\text{Si}}} \quad (3)$$

As shown in Fig. S2, the Au_2Si monolayer exhibits the robust stability on various substrates.

6 Dynamics stability of Au_2Si monolayer

For the thermodynamic stability of the Au2Si monolayer, the formation energy is the lowest when the rate of Si atoms is 1/3 as circled by the dark line in Figure S3. The formation energy is defined by

$$E_{\text{form}} = \frac{E_{\text{total}} - n_{\text{Au}}E_{\text{Au}} - n_{\text{Si}}E_{\text{Si}}}{n_{\text{Au}} + n_{\text{Si}}}, \quad (4)$$

where E_{total} is the total energy of the AuSi monolayer, $n_{\text{Au}}(n_{\text{Si}})$ is the number of Au (Si) atoms, and $E_{\text{Au}}(E_{\text{Si}})$ is the energy of Au

(Si) in the most stable bulk phase.

To check the dynamic stability of the Au_2Si monolayer, we have calculated the phonon dispersion to demonstrate the dynamics stability. The phonon dispersion was calculated by Phonopy code[5] using $3 \times 3 \times 1$ supercell. The phonon dispersion of these proposed structures are shown in Fig. S4(a). The top and side view of Au_2Si monolayer in free-standing form are shown in Fig. S4(b), (c).
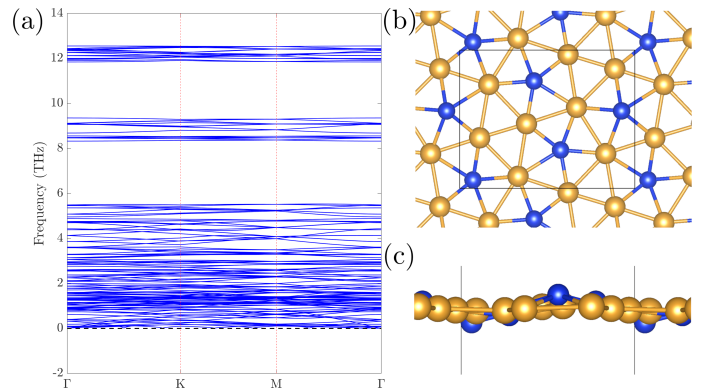

Fig. S4 The calculated phonon dispersion curves for the Au_2Si monolayer

Notes and references

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