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Strain-induced orientation of copper oxide nanoislands through decomposition of pre-organized copper nitrate①

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Abstract: By the decomposition of copper nitrate at 400 ℃, oriented islands of copperoxide crystals were successfully fabricated on the amorphous glass surface. X-ray diffraction (XRD), atom force microscope (AFM), and X-ray photoelectron spectroscopy (XPS) confirm the presence of copper oxide islands. The formation of oriented island structures is attributed to the following reasons: 1) the mismatch between the glass substrate and the copper oxide crystals during the relaxation of thermal expansion leads to the formation of islands; 2) the preorganized copper nitrate particles in the voids of colloidal crystals determine their ordered spatial distribution; 3) the strain of the glass substrate developing during calcination provides the driven energy for the orientation of copper oxide crystals along the same direction.

Key words: nanoislands; oriented growth; copper oxide; atom force microscope; colloidal crystals
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1 INTRODUCTION

Fabricating an array of nanosized islands on a solid support is expected to play a key role in the production of the next generation of electronic devices such as highly integrated circuits[1], quantum dot lasers[2], single electron transistors[3], and light-emitting diodes[4]. Copper oxide attracts great research interests owing to the properties of a large paramagnetic susceptibility at low temperature[5], p-type semiconductor with a narrow band gap[6], gas sensor and fundamental compound of some high-TC superconductor[7].

In the past, ordered arrays on a solid support were generally fabricated using some harsh approaches such as molecular beam epitaxy (MBE) and chemical vapor deposition(CVD)[8]. Among these harsh approaches, an important requirement is that the used substrates must have good crystal planes for the oriented growth of nanocrystals, such as the commonly used silicon (100)[9]. However, it is a challenge to process oriented arrays on an isotropic amorphous surface.

Here, a simple method was reported to fabricate oriented copper oxide islands on the amorphous glass surface through the decomposition of pre-organized copper nitrate. The organization of copper nitrate was realized by means of their permeation into the voids of assembled colloidal crystals. The deformation of the glass slides leads to the oriented growth of copper oxide crystals during the course of copper nitrate decomposition. XRD, XPS AFM were used to characterize the formed copper oxide on the glass surface.

2 EXPERIMENTAL

Monodisperse polystyrene spheres were synthesized using an emulsion polymerization. Before fabrication, the glass slides(1 cm × 1 cm) were soaked in the 3∶7(volum ratio) mixture of 30% perhydrol and 98% sulphuric acid for 12 h. After that, polystyrene latex particles with the average diameter of 500 nm were vertically cast onto the glass slides. They organized into a semi-opaque thin-layer by gravity sedimentation after the slow volatilization of the solvent. The layer thickness was controlled by the concentration of the latex.

Then 0.05 mol/L 2-propanol solution of copper nitrate was allowed to permeate into the voids in the colloid crystals. After exposed to the smooth nitrogen stream for 2 h, the glass slides were placed in the pipe heater and calcined (heating rate is 5 $K \cdot min^{-1}$) at 400 ℃ for 5 h. During the heating course, the two sides of these slides were fixed.

The calcined glass substrates were cleaned with benzene repeatedly and used as samples for the studies of XRD, XPS and AFM directly.

3 RESULTS AND DISCUSSION

A variety of techniques, such as selective wetting[10], and Langmuir-Blodgett films[11], can be used to form well-defined patterns on a surface. However, assembling the monodisperse colloidal spheres on an amorphous surface is a more simple method to

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realize the same aim[12]. By gravity sedimentation or centrifugation, monodisperse spheres can organize into close-packed three-dimensional (3D) arrays. Inorganic precursor, such as copper nitrate, can be filled into the voids in them. The subsequent chemical conversion and templates removing result in the formation of well-defined patterns[13].

Fig. 1 describes the possible routines of fabricating the copper oxide islands on an amorphous glass. By means of the capillary action, the 2-propanol solution of copper nitrate can easily permeate into the voids in the assembled colloidal crystals. Owing to its low interfacial energy (0.0217 N/m) compared with that of water (0.0738 N/m) and ethanol (0.0240 N/m), 2-propanol is a good solvent to keep the ordered structure of the colloid crystals. The liquid is expected to exist in the voids in the form of droplets due to the difference of interfacial tensions between polar nitrate solutions and weakly polar polystyrene. And the difference of the interfacial tension will lead to the gradual shrinkage of the droplets in the course of the solvent evaporation. After removing the solvent, well-defined pre-organized copper nitrate nanoparticles are anchored in the voids. Their spatial distribution should be identical to the inversion of the 3D ordered voids in space. Heating polystyrene and copper nitrate at 400 ℃, which is higher than both the glass transition temperature of the polymer(170 – 180 ℃) and the decomposition temperature of copper nitrate(300 ℃), leads to the decomposition of copper nitrate and thermal degradation of the polymer[14 – 16].

During the course of heating, the two unfixed sides of the substrate will generate thermal expansion along an opposite direction in space. The resulting strain provides the driving force for the crystal orientation, and hence, plays a critical role in the formation of well-defined patterns of copper oxide on the substrate[17]. Without the strain energy participating in the crystallization, it is impossible to obtain oriented crystals because there is no preferential orientation on such an isotropic amorphous surface. The application of strains has shown an effective means for the control of nanocrystalline orientation in the previous research[18].

The diffraction pattern of the as-prepared copper oxide is shown in Fig. 2. It can be indexed as monoclinic CuO (JCPDS Card NO. 45: 937). Three characteristic strong peaks correspond to its crystal planes of 110, 002 and 111, respectively. The broad diffraction line around 24° is caused by the amorphous glass and this amorphous property also affects the weak peaks of the other crystal planes of copper oxide such as 020, 220 and 310.

Fig. 3 shows the atom force microscope images of the as-prepared islands. Ordered arrays are obtained on the substrate through copper nitrate permeation into thin or thick colloidal crystals. The sizes of islands are characterized using two parameters: the height and the width of the base contacting with the surface of the substrate. In the case of a thin layer colloid, the forming islands are coherent. They are about 2.5 nm in height and 35 nm in width (Figs. 3 (a), (b)). The space of neighboring islands is about 40 nm. But for a thick layer, the islands with 3.7 nm in height and 200 nm in width present incoherent alignments and a decreased ordered degree (Figs. 3 (c), (d)). The neighboring space of about 300 nm is obviously larger than that of the coherent islands.

The formation of such island is attributed to mismatch between the substrate and the copper oxide in the relaxation of the thermal expansion. The stress arising from heating the substrate leads to the diffusion of atoms along the grain boundaries or through the lattices and thus leads to islands forming on the substrate[17]. The orientation of the islands along one direction is controlled by the dominant strain of the substrate along opposite direction in space.

The AFM images indicate that the layer thick-

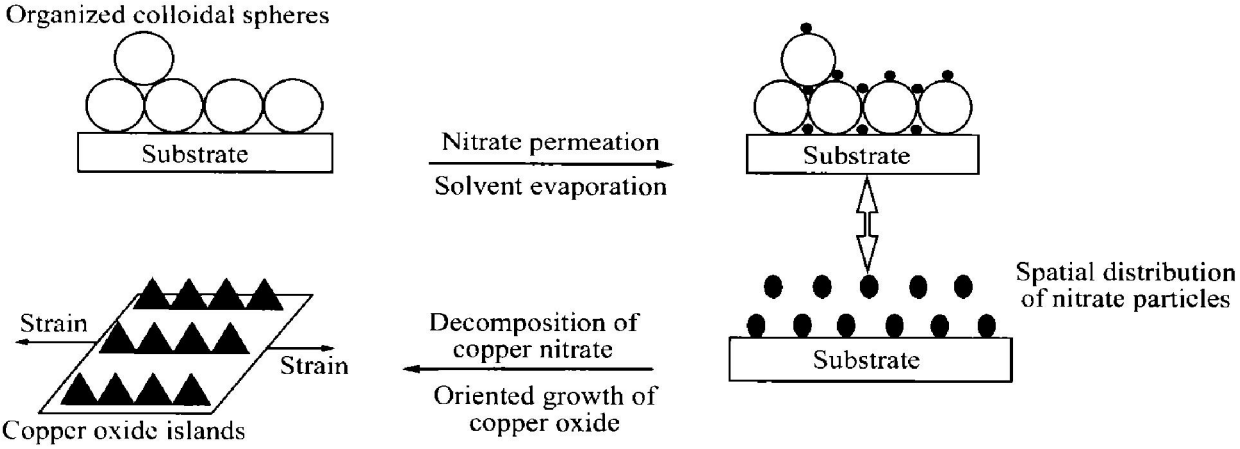

Fig. 1 Fabricating strategies of copper oxide nanoislands on amorphous glass slides

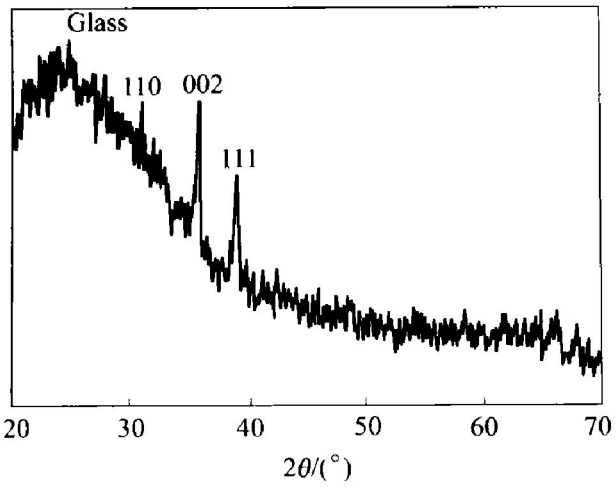

Fig. 2 X-ray diffraction pattern of copper oxide nanoislands on glass slides

ness is a critical factor to determine the width and height distribution of the islands on the substrate. When the colloids were heated at the temperature above their glass transition(T_g), they began to flow and result in the random shift of the voids that were filled with copper nitrate in space. This brings about bad influence on the spatial ordered distribution of the nitrate particles. Since there are no efficient measures to control the random shift of the voids, the ordered degree of the spatial distribution of the nitrate particles decreases in keeping with the increase of the thickness of the organized colloidal crystals. Additionally, because the degradation of polymers results in the shrinkage of the volume of the colloidal spheres, the adjacent space of the voids is shortened. So, the space of neighboring islands in two cases is both smaller than that of the pre-organized nitrate particles, which is identical to the diameter of an individual latex particle (about 500 nm determined by scan electron microscope). The forming mechanism of coherent and incoherent islands can be explained as follows. In the presence of thin colloidal crystal, the shift of pre-organized nitrate particles shortens their separation and thus they decompose into coherent islands. But too thick colloid will be filled by excessive mass nitrate particles and thus leads to the formation of dense oxide film in the region contacting with the substrate surface firstly. Subsequently, the remnant copper nitrate is not insufficient for decomposing into coherent islands.

It should be noted that these morphologies are not the microscopic reflection of the roughness of the glass surface because of its semi-sphere shaped disordered features observed in the experiments.

XPS is a powerful technique for studying the components of a surface layer and the results provide another evidence that island-like copper oxide covers on the surface(Fig. 4). The main peaks of Cu2p are observed at 933. 6 eV ($Cu2p_{3/2}$) and 952. 9 eV ($Cu2p_{1/2}$) with shake-up satellites at 942. 7 eV and 962. 4 eV. The existence of strong satellite features rules out the presence of Cu_2O phase[19]. The result of XPS is consistent with that of XRD. Besides, the

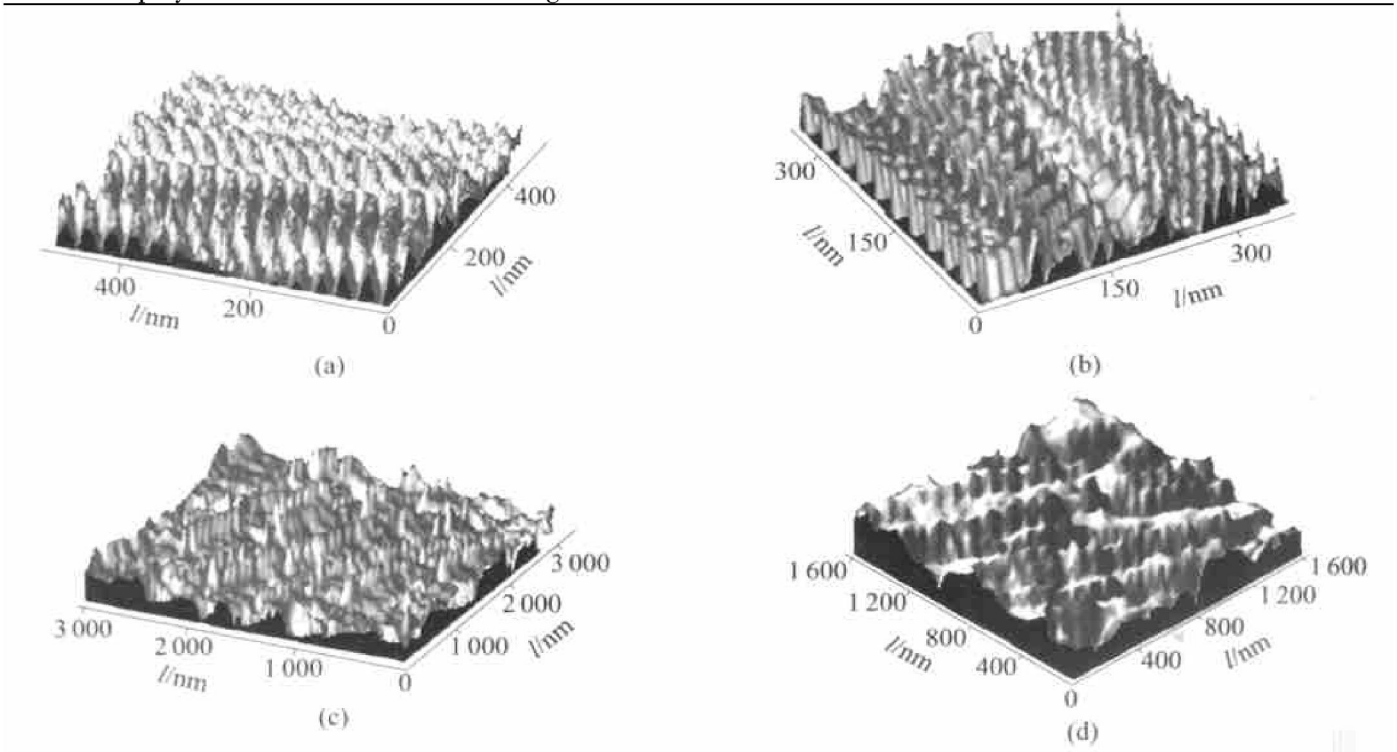

Fig. 3 AFM images

(a) —Coherent nanoislands of 500 nm × 500 nm; (b) —350 nm × 350 nm area controlled by thin colloids; (c) —Incoherent nanoislands of 3 000 nm × 3 000 nm; (d) —1 600 nm × 1 600 nm area controlled by thick colloids

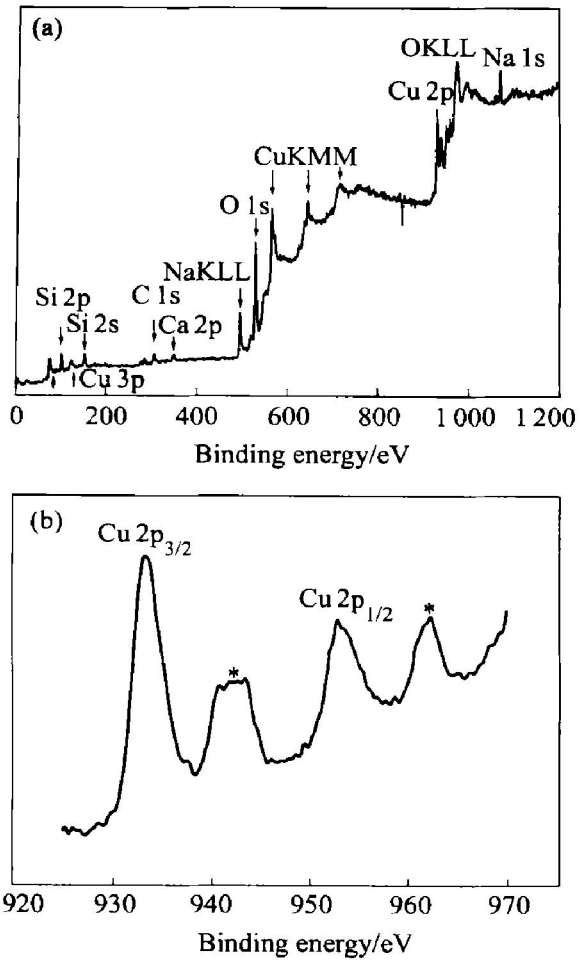

Fig. 4 XPS spectra of copper oxide nanoislands on glass
(a) —XPS survey spectrum;
(b) —Binding energy spectrum for Cu2p
* : Satellites

signals of Si, Ca, and Na, which are the components of the glass, exhibit in the survey spectrum. This result confirms that copper oxide islands form on the amorphous glass surface.

4 CONCLUSION

In conclusion, ordered arrays of copper oxide islands on an amorphous surface were prepared by the pre-organization and thermal decomposition of copper nitrate. The strain of the glass plays critical role in the oriented growth of copper oxide crystals. It is expected that this work provides a simple method to fabricate other islands on a similar surface.

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