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Prefer-oriented Cu_2O Micro-crystals: SAM Templated Growth and DMMP-vapor Detection

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Abstract: With self-assembled monolayer (SAM) as template, cubic cuprous-oxide (Cu_2O) crystals with preferred orientation are obtained *via* simple and effective electrochemical redox process. Micro-region X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to characterize the as-grown Cu_2O crystals. Besides uniform morphology and crystal size, the micro-crystals take preferred orientation that is strongly influences by the pre-modified SAM on substrate. The experiments indicate that the SAM not only acts as the growing template for the crystals, but also strongly affects the electrochemical redox process. To explore its sensing properties, the Cu_2O crystals were grown onto a micro-cantilever to detect DMMP (dimethyl methylphosphonate) vapor. The sensing mechanism is complexation of phosphonyl group with Cu(I) that generates surface-stress at the cantilever surface. Tens of ppb DMMP vapor is reproducibly detected.

Key words: cuprous oxide; preferred orientation; electrochemical redox; self-assembled monolayers; gas sensor

Morphology of micro/nano-structures has direct influence on their conspicuous physical/chemical properties, which makes it very important to control syntheses of the micro/nanomaterials to get ordered crystals in orientations and uniform shapes[1]. Extensive studies have been devoted to the controllable crystallization in the dimension of micro/nano scale. In particular, there has been growing interest in cuprous oxide. As a p-type semiconductor with direct band-gap of 2.17 eV, Cu_2O features excellent optical, sensing, catalytic and magnetic properties[2-3]. Efforts on shaped-controlled synthesis of cuprous oxide micro/nano-crystals have been made due to great research interest[4-5]. Among various crystal engineering approaches, the ability to functionalize a surface with the desired properties and their highly ordered structures make self-assembled monolayers (SAMs) attractive templates for nucleation and crystal growth[6]. It has been reported that the SAM can act as a template to guide nucleation and growth of crystals like calcite[7], ZnO[8], organic molecules[9] and glycine[10]. Although the previous works offered a certain level of control over crystal orientation, the grown crystals were often diverse in sizes and shapes within a single sample. Multiple controls over combined properties are still challenging.

Herein we utilized a combination of two methods, SAM templating and electrochemical redox, which provides control over multiple parameters of crystallization. Micro/nano crystals of Cu_2O with preferred crystal orientation, uniform morphology and crystal size were synthesized for the first time. The as-obtained crystals feature good sensing property to DMMP (dimethyl methylphosphonate) vapor.

1 Experimental

A specifically designed chip for electrochemical crystallization process is schematically shown in Fig. 1 and described as follows. After 300nm-thick SiO_2 is thermally grown on (100) silicon wafers, 30 nm Cr and 100 nm Au composite film is deposited on the wafer front-side by using electron-beam evaporation. Square-shaped Au plates are patterned by photolithographic process and wet metal etching technique. Subsequently, a 500nm-thick Al film is electron-beam evaporated on top of a patterned photoresist layer and, then, lift-off process is used to form the square-ring shaped Al pads. It can be seen in Fig.1 that, the Al pad is at the surrounding of the Au pad with an overlapping inter-contact area while the central part of the Au

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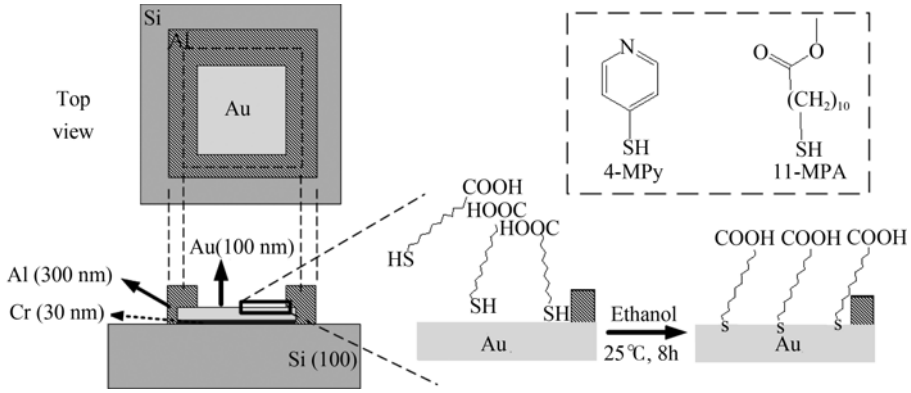

Fig. 1 Schematics showing the configuration of the micro-fabricated chip and the processes of the SAM modification on the chip surface

The top-right inset shows the chemical structures of the thiol compounds for the formation of the SAMs on gold surface

pad is exposed. The size of one unit is 500 μm×500 μm.

The modification process of the thiol SAM on gold is described as follows: prior to modification of the chip with thiol SAM, the gold-pad substrate should be carefully cleaned. We firstly clean the chip with acetone, absolute ethanol, deionized water for several times each, and then pretreat the chip with Piranha solution (7:3, 98% H_2SO_4/30% H_2O_2) for 5 min. Upon removal from the Piranha solution, the chips are rinsed with deionized water and absolute ethanol for two times each. The SAM on the gold surface of the chip is formed by immersing the freshly cleaned chips into 2 mmol/L solution of the thiol compounds in absolute ethanol for about 8 h.Two kinds of SAMs are modified on different chips, by soaking the chips in 2 mmol/L ethanol solutions of 11-mercaptoundecanoic acid (11-MUA, Aldrich) and 4-mercaptopyridine (4-MPy, Aldrich) for about 8 h, respectively. The samples are subsequently rinsed with ethanol and deioned water to remove the residues.

With the modified SAM on gold surface, the chip samples are sequentially put in aqueous solutions of 2 mmol/L $CuSO_4$ for electrochemical crystallization. The electrochemical-based crystallization process is implemented at room temperature for various periods of time from 5 min to several hours to inspect the different stages of the crystallization. After completion of the crystallization processes, the samples are rinsed with deioned water to remove the residues and dried in ambient lab air. The as-grown crystals on top of SAM are characterized with field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700, 10 kV), micro-region X-ray diffraction (XRD, Rigaku, Dmax2550) that is operated at 40 kV and at the current of 40mA with Cu Kα radiation.

2 Results and discussion

Typical FE-SEM images of the resulting products are illustrated in Fig. 2. As is shown in Figs. 2(a) and (b) where the used substrates are pre-modified with the SAMs of 11-MUA and 4-MPy, respectively, size-uniformed micro-cubes are grown on top of the SAMs. Figure 2(a) presents {111}-plane particles, which has the <111> axis perpendicular to the substrate. Figure 2(b) presents {110} crystals; in this case, the axis perpendicular to the substrate is <110>. Therefore, preferred orientations against the substrate have been noted. In control experiment, where bare Au surface is used, the surface precipitate represents a disorder surface state with various crystal sizes (Fig. 2(c)).

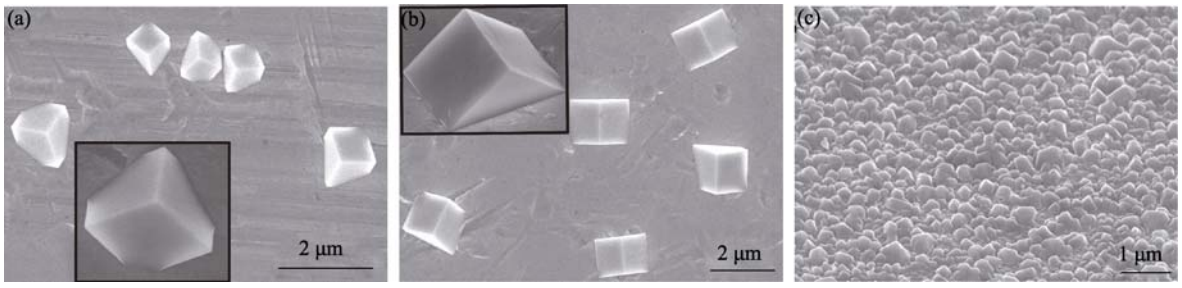

Fig. 2 FE-SEM images showing the orientations of the Cu_2O crystals on top of the SAM top of 11-MUA (a), on top of 4-MPy (b), and on bare gold surface (c)

The insets in (a) and (b) show the close-up views of the oriented crystals

The micro-region XRD analysis results in Fig. 3 show that the as-obtained products on top of the SAMs can be indexed to the cubic Cu_2O (JCPDS, 05-0667). As is shown in Fig. 3, the sharp peaks indicate that Cu_2O crystals feature high crystallinity and purity. For the crystals grown on top of the SAM terminated with –COOH groups, a preferred (111) crystal plane is indicated by the relatively strong (111) peak (Fig.3). If the pre-modified SAM is terminated with pyridine groups (–Py), the preferred crystal plane changes to (220), as is shown in the line (b) of Fig. 3.

The formation of as-obtained Cu_2O crystals involves two procedures: SAM templating and electrochemical redox. The SAM templated electrochemical crystallization is schematically shown in Fig. 4.

The thiols are well known to form an orderly structured high-coverage monolayer on Au (111) lattice with a title angle in the range of 30°–50°[11]. Subsequently, the terminals of the SAM selectively coordinate with Cu^{2+} ions, and cause the lack of mobility of Cu^{2+} ions at the surface layer. The electrochemical redox is based on the following equations. The electrons transfer from Al to Au due to direct connection. The precipitation of Cu_2O occurs at the third step (Eq. (3)).

$$\text{At anode: } Al(s)= Al^{3+}(aq)+3e^- \quad (1)$$

$$\text{At cathode: } Cu^{2+}(aq)+e^-=Cu^+ \quad (2)$$

$$2Cu^++H_2O=Cu_2O(s)+2H^+ \quad (3)$$

The electrons from Al transfer to Au surface, through SAM layer, to the coordinated Cu(II) layer, where the electrochemical reduction of Cu(II) to Cu(I) takes place. Beginning from the location fixed Cu(I) layer, the crystallization of Cu_2O occurs. The contacting crystal plane is established at the SAM/crystal interface that further leads to the distinct orientation of the grown crystals. The difference in orientations of the crystals can be attributed to the different coordinate capability of the SAM functional group with Cu^{2+} and the different geometries of the SAMs. The complexation of Cu(II) with –COOH or –Py group is a key process to determine the preferred orientation. While Au surface is modified with –COOH terminated SAM, one –COOH group coordinates with one Cu^{2+} ion. As the geometry of the highly-ordered SAM is similar to the geometry structure of the Au (111) surface, the preferred orientation of Cu_2O on –COOH terminated SAM surface is identical to the Cu_2O deposited on Au. In the case of –Py group, two –Py groups coordinate with one Cu^{2+} ion, which determines the geometry of the coordinated Cu(II) plane. Thus, the specialized geometry of the nucleating plane further leads to form the (220) oriented Cu_2O crystals. Therefore, with the surface chemistry property that leads to specific intermolecular interactions with the nucleating plane of crystals, their morphology and crystal form is thereby controlled.

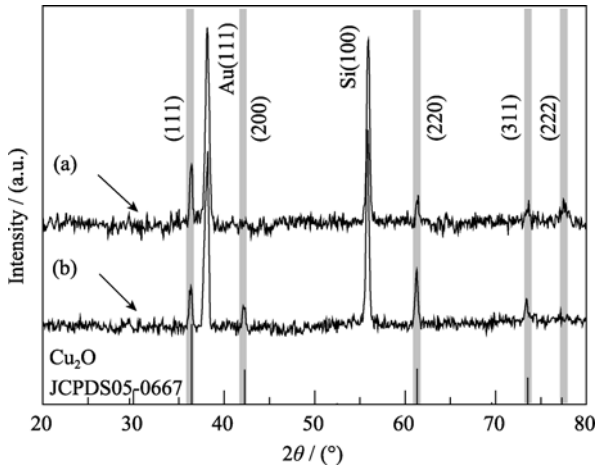

Fig. 3　Micro-region XRD patterns of Cu_2O crystals produced on top of the SAM
(a) 11-MUA; (b) 4-MPy

Unlike the previously reported crystallization methods using SAMs as templates[7-10], herein the SAM template is also experimentally found to have strong influence on electrochemical reduction process by acting as an electron transfer barrier[11]. During the electrochemical reduction process, the electrons have to transfer through the SAM to start the reduction. The reduction process is therefore controlled by the property of the SAM, which is the key step of crystallization. This offers opportunities of control over the crystal sizes. It is experimentally verified that for as-grown Cu_2O in the same processing time, the crystal sizes are approximately the same. The experimentally recorded size evolution of the growing crystals in terms of the processing time with 11-MUA SAM as the barrier layer is shown in Fig. 5. According to our experimental observation, no crystal can be grown within the first 60 min. In control experiments, where bare Au (without SAM as electron transfer barrier) was used as the substrates, disordered Cu_2O with various sizes were observed within 15 min. It is worthy pointing out that when the crystal size gets larger than several microns, defects begin to appear in the crystals (typical crystal see Fig. 6). The defects cause void in the crystal body while the ribs remain well structured.

Using this combination method of SAM templating and electrochemical redox, a homogenous layer of Cu_2O crystals is prepared, which shows great potential in gas sensing. Static micro-cantilever[12] as platform to investigate the sensing performance is used of as-obtained Cu_2O microcrystals (11-MUA templated) to DMMP (a simulant of nerve agent sarin) vapor. The specific adsorption of DMMP vapor due to the complexation of a phosphonyl group with as-grown Cu_2O crystal layer induced surface stress change

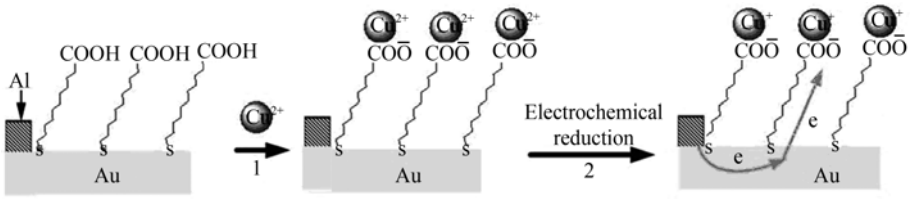

Fig. 4 Schematics showing the SAM templating effect during the Cu_2O crystal growth

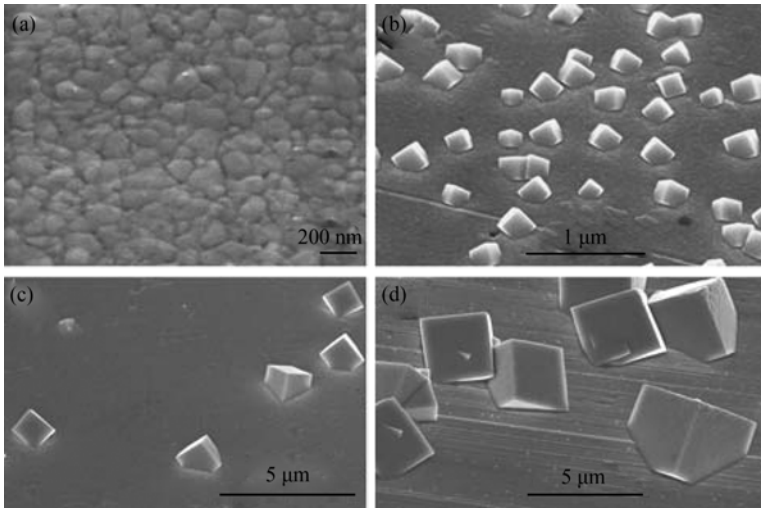

Fig. 5 FE-SEM images recording the morphology evolution of the Cu_2O crystals grown on 11-MUA SAM at different growing stages
(a) <1 h; (b) 1–3 h; (c) 4–6 h; (d) >6 h

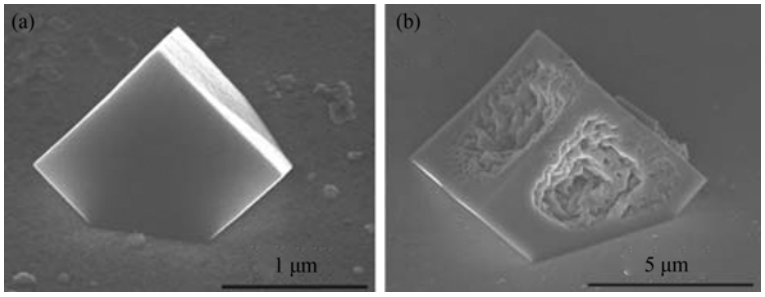

Fig. 6 FE-SEM images showing the defects of Cu_2O crystal cube grown on SAM 11-MUA
(a) Small well-defined crystal cube; (b) Big crystal cube with defects

of the cantilever[12-13], which was also detected by integrated piezoresistive readout system as response voltage change. The gas sensing responses of the Cu_2O micro-cubes based sensors were shown in Fig. 7. Good reversibility and re-producibility of the gas sensor was observed for detection of tens ppb DMMP vapor at room temperature.

3 Conclusions

The highly controlled synthesis of Cu_2O with uni-form nucleating plane, size, and morphology are demonstrated by combining the SAM-induced oriented crystallization with electrochemical redox. The as formed homogenous Cu_2O crystal layer showed a good sensing response to DMMP vapor on the tens of ppb level. This method not only provides oriented Cu_2O crystals with good gas

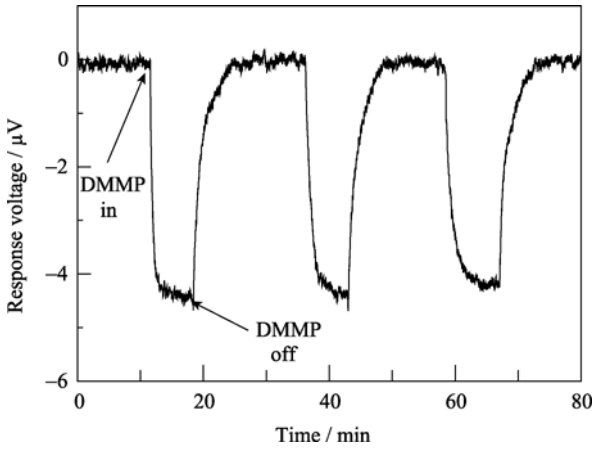

Fig. 7 Three-time continual detections showing reversible and reproducible response of the Cu_2O modified sensor to DMMP vapor of 50 ppb

sensing properties, but also offers great opportunity for the controlled synthesis of micro-/nanostructures. The advantages to control over multiple parameters of crystallization makes this approach suitable for studies of surface morphology, and is valuable in crystal growth. Therefore, we suggest, that the use of the templating by SAM modified surfaces together with specialized electrochemical growth proposes a promising chemical route to yield high-level control of multiple parameters of crystallization in one experiment.

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自组装单层膜模板控制生长氧化亚铜晶体及其对 DMMP 气体的检测

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摘 要: 使用了一种在自组装单分子层(SAM)模板衬底上由电化学氧化–还原自发生长的方法, 择优取向生长氧化亚铜(Cu_2O)微晶. 通过扫描电子显微镜和微区 XRD 等方法对合成的 Cu_2O 晶体进行了形貌和结构表征. 结果表明: 合成的样品为立方结构的 Cu_2O 晶体, 且形貌、取向和颗粒尺寸得到了有效控制, 此结果可归结为 SAMs 对电化学氧化–还原过程的影响和结晶过程中的模板效应. 利用该方法, 将 Cu_2O 晶体生长于静态式微悬臂梁的表面作为敏感层, 制得了一种新型的化学传感器. 基于 Cu_2O 晶体表面的 Cu(I)与 DMMP (甲基膦酸二甲酯, 沙林模拟剂)分子中的膦酰基团之间存在的配位作用, 该传感器可对几十 ppb 的 DMMP 重复响应.

关　键　词: 氧化亚铜; 择优取向; 电化学氧化还原; 自组装单分子层; 气体传感器

中图分类号: TQ174; O782　　**文献标识码:** A