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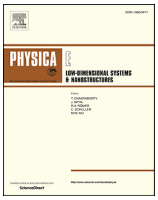

Enhanced field emission properties of the copper sulfide nanowalls with optimized 3-D morphology

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ABSTRACT

The three-dimensional (3-D) copper sulfide nanowalls with sharp edges were successfully prepared by one-step anodization method. An interesting finding was that the morphology and microstructure of 3-D copper sulfide nanowalls can be regulated and optimized by abjusting the anodization time, and the corresponding field emission (FE) characteristics were significantly improved. The value of turn-on field can be dramatically reduced from 11.84 to 2.84 V/μm and the field enhancement factor up to 19899. Besides, the optimal 3-D copper sulfide nanowalls showed a long-term thermal stability and better conductivity. Preliminary researches indicate that as a promising field emitter, the 3-D copper sulfide nanowalls have potential applications in the field of vacuum micro- or nano-electronic devices.

1. Introduction

In recent years, owing to its excellent physical and chemical properties, such as high electronic conductivity, good capacitive performance, sensitive chemical-sensing, high absorption coefficient etc. [1–4], the copper sulfide nano-powders (nanoparticles, nanoflowers, nanosheets etc.) [5–7] have been widely studied by many researchers in the field of lithium-ion batteries, photovoltaic cells, photocatalysis, sensor, supercapacitor etc. [8–13]. However, to date there is little work on the investigation of field emission by using the copper sulfide nanostructures.

In order to seek desirable field emitters, what the researchers made many effective efforts for many years can be summarized as two respects: one is to discover and synthesize new materials with excellent field emission performance; another is to design and fabricate the corresponding field emitters with optimized morphologies and structures. As we recently noted, as one of metal chalcogenide semiconductors, copper sulfide (Cu_xS, $x = 1, 2$), with a narrow band gap (1.2–2.74 eV) [14] can not only meet the field emitter high electrical conductivity requirements for efficient electronic transport, but also fit its lower work function need (Cu_2S $\varphi = 5.3$ eV [15], CuS $\varphi = 4.95$ eV [16]), compared with other metal oxide semiconductor field emitters such as ZnO ($\varphi = 5.3$ eV) [17], Fe_2O_3 ($\varphi = 5.6$ eV) [18] and CuO ($\varphi = 5.2$ eV) [19]. In other words, the electrons can more easily escape from the Cu_xS surface barrier than that of metal oxide. In the regard, the copper sulfide (Cu_xS, $x = 1, 2$) should be a new promising candidate for field emitter materials.

Of course, to get a favorable field emitter, apart from caring the electric characters of Cu_xS we should also carefully consider how to design and manipulate its geometry structure, because theory and experiment both show that the field electron emission driven by strong local electric field largely depends on the apex curvature radius of emitter and the layout of the emission sites. Obviously, various nano-powders of copper sulfide obtained by many methods, such as super cooling chemical vapor deposition [20], elemental direct reaction [21], could not meet the requirements selected as a field emitter. Therefore, it is necessary taking some new strategies to design and fabricate suitable Cu_xS field emitter instead of its powder state. Based our previous related research experience, we consider to construct the vertically aligned sheet-like Cu_xS nanoarray films with large area and three-dimensional (3-D) uniform distribution by electrochemical anodization method. For convenience narration, we will call this form of copper sulfide nanostructures as 3-D copper sulfide nanowalls in this article. What we expected was that this designed 3-D copper sulfide nanowalls could not only preserve the character of the large field enhancement factor, but also possess superior heat dissipation ability compared to other shaped field emitters.

Based on the above considerations, in this article, the 3-D copper

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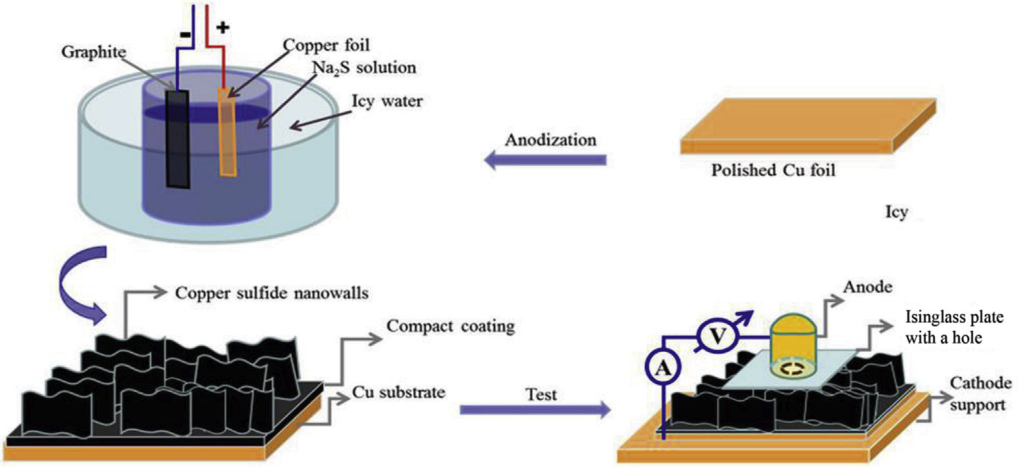

Fig. 1. Schematic of the growth process for the 3-D copper sulfide nanoplates.

sulfide nanowalls have been successfully prepared by a one-step electrochemical anodization method. As anticipated, the vertically aligned Cu_xS nanowalls tightly grew on the copper substrate, and showed a large area of three-dimensional uniform distribution. By adjusting anodization time, the morphology and microstructure of the samples could be easily regulated and optimized, which led to the value of turn-on field dramatically reduced from 11.84 to 2.84 V/μm. More importantly, the optimized samples both had a large field enhancement factor, and exhibited an excellent FE stability. Preliminary researches suggest that the 3-D copper sulfide nanowalls, as a promising field emitter, would have potential value in the field of vacuum micro- or nano-electronic devices.

2. Experimental

2.1. Synthesis

With Na_2S solution as the electrolyte, copper sulfide nanowalls were prepared by a forthright galvanostatic anodization. Firstly, high purity Cu foils (99.999%, 10 mm × 20 mm × 0. 2 mm) were cleaned with acetone, ethanol, deionized water in sequence, next the Cu foils were polished with 1.0 M HCl in an ultrasound bath for 3 min and washed several times by deionized water then dried in air at room temperature. Then the cleaned Cu foil was immersed in 1.5 M Na_2S anodizing electrolyte solution as an anode and the graphite was the cathode of the anodization system. Next the copper sulfide nanowalls were grown by oxidizing the Cu sheets in a galvanostatic anodization system at 10 mA for different duration of 5, 10, 13, 15, 17 and 21 min, respectively, at 0 °C. Lastly, after washing with distilled water for several times, the obtained samples were dried in air at room temperature.

Schematic of the growth process of 3-D copper sulfide nanowalls and the testing is shown in Fig. 1.

2.2. Characterization

The obtained samples were analyzed by a field emission scanning electron microscopy (FESEM; ZEISS, ULTRA plus, operation at 5.0 kV) equipped with an X-ray energy dispersive spectroscope (EDS). The microstructure and crystallinity were examined by a transmission electron microscope (TEM, Tecnai-G2-F30, operated at 300 kV) matched with corresponding selected area electron diffraction (SAED) pattern and remarked with X-ray diffraction (XRD) using a Rigaku D/max-2400 diffractometer (with Cu-Kα, $\lambda = 0.154056$ nm radiation at 40 kV and 150 mA). The test equipment and method of the FE properties were the same as in our previous work [17]. The emission current was measured under varying applied voltages (up to 2000 V).

3. Results and discussion

Fig. 2 shows the surface and section morphology and geometry structure of the 3-D copper sulfide nanowalls anodized for 5, 10, 15 and 21 min, respectively. It can be seen that the vertically aligned copper sulfide nanowalls with the sharp edges and rugged folds show a large area of 3-D uniform distribution and tightly grow on copper substrate forming reliable electric contact. Meanwhile, the subtle morphological evolution from the images of Fig. 2 also reveals that the anodization time can manipulate the morphology and microstructure of 3-D copper sulfide nanowalls. And the detailed statistics for the morphological evolution with anodization time are shown in Fig. 3. In which the conclusive analysis of the data leads out the following rule: with the prolonging of anodization duration (5–21 min) the thickness of nanowall edges varies in a wide range from 5 to 98 nm as shown in Fig. 3(a–d), and the statistical average values of thickness present a thinning trend (81.4–19.4 nm) as seen in Fig. 3(e), but the nanowalls section length (or the film thickness) has an increased trend (2.7–11.4 μm) as shown in Fig. 3 (f).

The XRD pattern in Fig. 4 shows the crystal phase composition of the 3-D copper sulfide (Cu_xS, x = 1, 2) nanowalls anodized for 15 min in 1.5 M Na_2S solution. All diffraction peaks from the sample can be well indexed to the crystal phases of chalcocite (Cu_2S, JCPDS 83-1462) and covellite (CuS, JCPDS 75-2236, 78-0878). In order to further investigate the crystal phase composition, Fig. 5 provides the related data revealed by TEM, SAED and element maps. In Fig. 5(a and b) the TEM image and SAED pattern of Cu_xS nanowalls indicate that the copper sulfide nanowalls are polycrystalline substance. Having further zoomed in on the sign (1) and (2) of Fig. 5(b), some clear lattice fringes could be observed from Fig. 5(c and d). Here there are two sets of lattice fringes with spacings of 0.27 nm and 0.195 nm, the two differentiate correspondingly in the (006) and (101) plane of covellite CuS and chalcocite Cu_2S, which are in agreement with the data from other literature [22,23]. And the element maps in the Fig. 5(e and f) reveal that the nanowalls consist of Cu and S two elements. To be sure, the results of TEM are also in concert well with the analysis of XRD in Fig. 4.