Solution-Processed p-Type Transparent Conducting $BaCu_2S_2$ Thin Film

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Received January 25, 2007
Revised Manuscript Received April 12, 2007

Because of the fundamental role they would play in the promising invisible electronic devices, p-type transparent conducting materials (TCMs) have attracted considerable attention ever since the first reported one, $CuAlO_2$, in 1997.[1] Many efforts have been dedicated to them thereafter, and a series of novel p-type TCMs have been reported, such as nitrogen-doped ZnO,[2] $CuMO_2$ (M = Ga, In, Sc, and Y),[3−6] $SrCu_2O_2$,[7] LnCuOQ (where Ln = lanthanide and Q = S, Se, Te),[8−10] $CuAlS_2$,[11] $BaCu_2S_2$,[12] BaCuQF (Q = S, Se),[13] and so forth. However, the general properties of p-type TCMs are still not able to meet the basic demand of the actual applications. According to Zunger's theory, complex sulfide semiconductors may be the most appropriate candidates for TCMs, because of the tradeoff between the forbidden band gap and the position of valence band maximum (VBM).[14] The band gap directly reflects the transparent properties of TCMs, while the position of VBM indicates the aptness for the type of electrical conduction (p-type or n-type). Compared with oxides, the VBMs of complex sulfide semiconductors are much closer to the vacuum level, favoring the occurrence of p-type conduction. Besides, the bandgaps of many complex sulfide semiconductors are wide enough to accommodate the transmittance of visible light.

Along with the issue of pursuing higher-performance p-type TCMs (higher conductivity and better transmittance in the visible-light region), the practical cost of a technically feasible deposition technique for p-type TCM thin films is another important one to be considered. As opposed to the conventional vacuum processes and vapor-phase deposition methods employed for nearly all of the p-type TCM thin films,[1−12] the solution-based process offers substantial cost reduction and favors a high throughput for the fabrication of p-type TCM-based devices. However, the typically poor solubility of such covalently bonded inorganic materials imposes a severe obstacle to overcome. Fortunately, the method employing anhydrous hydrazine as a solvent for chalcogenides and subsequently spin-casting the hydrazine-based chalcogenide solution into thin films, as reported by Mitzi et al. in 2004,[15] is a convenient and versatile path to high-quality chalcogenide thin films. It introduces no pollutants to the targeted products, the films can be deposited at a moderately low temperature (<350 °C), and a series of achievements of the method have been realized.[15−20] As the most appropriate p-type TCM candidates are the wide band gap complex sulfide semiconductors, the significance of such a solution-based process bulks up greatly, for it may offer a strong impetus to the success of p-type TCMs. However, the very low solubility of some chalcogenides in anhydrous hydrazine, even with excess additional corresponding chalcogens, restricts the application of such a convenient thin-film-deposition method. Here we propose a new technique, the high-temperature refluxing, to overcome such an obstacle and to further broaden the applicability territory of such a solution method. We demonstrate the deposition of the first p-type transparent conducting $BaCu_2S_2$ thin film employing the solution deposition strategy. The careful investigation of electrical and optical properties was also conducted.

$BaCu_2S_2$, one of the typical p-type TCMs reported by Keszler et al.,[12] shows fair comprehensive transparent and conducting properties. $BaCu_2S_2$ has two forms, the low-temperature orthorhombic phase (α-$BaCu_2S_2$, *Pnma*) and the high-temperature tetragonal phase (β-$BaCu_2S_2$, *I*4/*mmm*). The highlight of the structure character of the low-temperature orthorhombic phase containing the short Cu···Cu distance (2.71 Å) implies the existence of some strong interaction between two Cu atoms. So, the enhancement of mobility and therefore the associated conductivity can be expected.[12] The α-$BaCu_2S_2$ thin film has been deposited by the radio

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10.1021/cm070235a CCC: $37.00 © 2007 American Chemical Society
Published on Web 05/27/2007

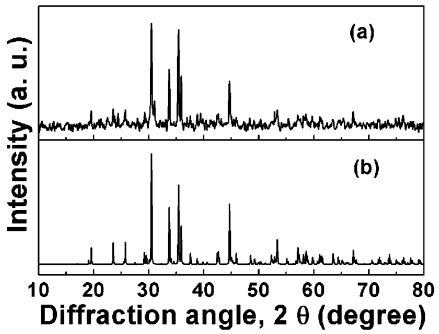

Figure 1. (a) X-ray diffraction pattern of bulk $BaCu_2S_2$ powder, prepared by first distilling the precursor solution at 110 °C and then decomposing the obtained precursor powder at 300 °C, both under argon atmosphere. (b) Standard X-ray diffraction pattern of $BaCu_2S_2$ *Pnma* phase from JCPDS entry no.79-1646.

frequency (rf) sputtering method; however, the conductivity of the film is only about 17 S cm^{-1}.[12] The low conductivity may be resulted from the S-vacancies in the film, for the low sulfur vapor pressure in the deposition chamber induced the excess volatilization of sulfur. The S-vacancies could be ionized and acted as donor, offsetting the already existing holes, leading to the decreasing of carrier concentration, and so does the conductivity.

Unlike the previous reported chalcogenide systems (SnS_2, $SnSe_2$, In_2Se_3, In_2Te_3, ZnTe, and Cu_2S)[15−20] and alkali chalcogenides, BaS cannot dissolve completely into the solvent anhydrous hydrazine with additional sulfur by simply stirring at room temperature, even with plenty of excess anhydrous hydrazine (0.1 mmol BaS in 10 mL of anhydrous hydrazine), and more additional sulfide added in hydrazine was proved to be ineffective, as well. *Caution: anhydrous hydrazine is highly toxic and should be handled carefully without exposition to either the liquid or the vapor*. However, a long-time (24 h) and high-temperature (180 °C)[21] refluxing of the nominal solution could result in a denser concentration of BaS solution, up to 0.49 mmol/mL.[22]

A mixture of the pale yellow BaS solution (filtered through a 0.2 μm syringe filter) and Cu_2S solution (prepared according to Mitzi et al.'s method)[15] is stable for weeks (6 weeks in the test, longer time testing was not considered for the current experiment) under inert atmosphere (nitrogen, argon), which was employed as a precursor solution to the targeted $BaCu_2S_2$ semiconductor. It was verified to be feasible by removing solvent hydrazine from the mixture at 120 °C, followed by heat treatment at 300 °C for 30 min. The harvested powder product was dark-red, and it was identified to be $BaCu_2S_2$ *Pnma* phase by powder X-ray diffraction (Figure 1).

To prepare the film, silica glass was used as substrates, which were cleaned using a soap scrub/rinse, followed by a piranha process (4:1 concentrated sulfuric acid to hydrogen peroxide). One drop of the mixed solution was placed on the substrate and spin-casted into film at 3500 rpm for 40 s, after a pre-spin at 150 rpm for 3 s. The whole process was performed in a glovebox with the concentration of O_2 and H_2O maintained under 0.1 ppm. The spin-casted precursor thin film was immediately transferred to the tube furnace with air pre-driven by inert gas Ar, followed by subsequent heat treatment, and the temperature was set at 300 °C for 4 h with the heating rate of 5 °C min^{-1}. The precursor film was chemically converted to the targeted semiconductor $BaCu_2S_2$, as confirmed by the high-resolution transmission electron microscopy (HRTEM) image (Figure 2a). The average spacing between the paralleled fringes is about 2.93 Å, which is consistent with the distance between the (211) planes of $BaCu_2S_2$ *Pnma* phase. Furthermore, the electron diffraction rings can be completely indexed according to the structure of the $BaCu_2S_2$ *Pnma* phase (see Supporting Information). The bird's eye view scanning electron microscopy (SEM) image (Figure 2b) of the thin film indicates that the film was poorly crystallized, and the texture of the film was somewhat coarse. The poor crystallinity of the film may be caused by the low-temperature treatment, while the roughness of the film may be resulted from the poor wetting ability of the $BaCu_2S_2$ solution to silica substrates. The thickness of the film was evaluated to be about 100 nm from the cross-sectional SEM image (see Supporting Information).

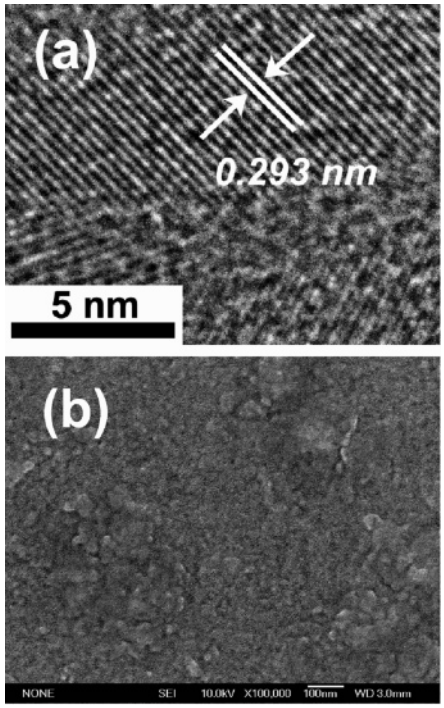

Figure 2. (a) HRTEM image of the $BaCu_2S_2$ thin film. (b) Bird's eye view SEM image of the $BaCu_2S_2$ thin film.

The as-prepared thin film is light yellowish brown; its transmittance spectrum is shown in Figure 3. It can be observed that the average transmittance in the region of 500−800 nm is about 75%. The inset shows a plot of $(\alpha h\nu)^2$ versus $h\nu$, from which the direct allowed band gap can be estimated by using extrapolation methods; it is found to be about 2.47 eV. This value is lager than the reported value (2.3 eV). The blue shift may result from the quantum size effect (the grain size of the film was evaluated at about 5−10 nm) and Möss−

(21) The refluxing temperature was gradually raised up to 180 °C after a 12 h refluxing at 110 °C. Raising the temperature directly to 180 °C can be very dangerous.

(22) Anhydrous hydrazine in 10 mL of hydrazine-based BaS solution was removed at 120 °C, and the residue was heat treated at 500 °C for 2 h. The accurate weight of the haversted pale yellow powder was determined, and the actual concentration of BaS solution was deduced.

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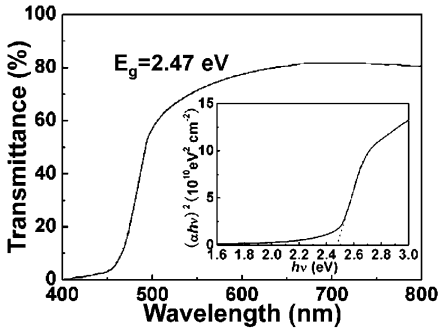

Figure 3. Optical transmittance spectrum of the $BaCu_2S_2$ thin film. The inset shows a $(\alpha h\nu)^2-h\nu$ plot for the estimate of an energy gap of direct character

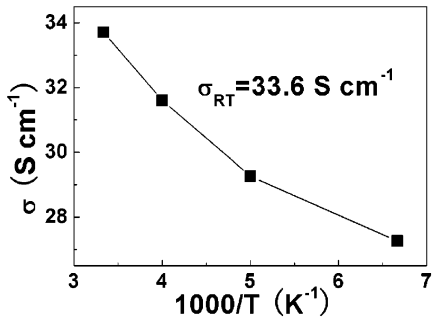

Figure 4. Reciprocal temperature dependence of electrical conductivity of the $BaCu_2S_2$ thin film.

Burstein effect (the carrier concentration was measured to be 4.29×10^{20}/cm^3).

Electrical measurement was conducted with an Accent HL5500 Hall System. P-type conducting was confirmed by the positive results of both the Hall coefficient (2.96×10^{-2} cm^3 C^{-1}) and the Seebeck coefficient (51 μV K^{-1}) at room temperature. The reciprocal temperature dependence of the electrical conductivity of the $BaCu_2S_2$ thin film is illustrated in Figure 4, in which the typical semiconductor conducting behavior can be observed. Electrical conductivity of the film at room temperature was measured to be 33.6 S cm^{-1}, almost two times as high as the reported value,[12] and exceeds the room-temperature conductivities of those typical Cu-contained *p*-type TCMs, 5.0 S cm^{-1} for the $CuAlO_{2+x}$ film[23] and 20 S cm^{-1} for the Sr-doped LaCuOS film.[24] The enhancement of the conductivity can partially be attributed to the high concentration of the ionized point defects, such as V''_{Cu},[25] acting as acceptors. What is more, as stated above, the additional sulfur in the precursor thin films and low-temperature heat treatment prevented the excess volatilization of sulfur in the targeted films, and the formation of hole killers, S-vacancies, was suppressed. So, high carrier concentration can be realized, as measured to be 4.29×10^{20}/cm^3 at room temperature, leading to the fair increase in conductivities. Hall mobility of the film was measured to be 0.49 cm^2 V^{-1} s^{-1}, which is much lower than that of the film prepared by rf sputtering. The reduction of the mobility may result from the poor crystalline nature of the film and the associated defects.

In summary, we have successfully prepared the α-$BaCu_2S_2$ thin films by spin-coating. Further, we found that high-temperature refluxing is of fair advantage to the solubility of chalcogenides in hydrazine, and it can be expected that other examples of hard-to-be-dissolved chalcogenides might also be spin-casted into films by this technique. Generally, the present successful experiment implies that the applicability of such a hydrazine-based solution to the chalcogenide thin film method can be further expanded. The as-prepared α-$BaCu_2S_2$ thin film shows an excellent p-type electrical conductivity (33.6 S cm^{-1} at room temperature), almost two times as high as the reported value,[12] and a fair transmittance in the region of visible light (about 75% transmittance in the region of 500−800 nm). The promising transparent and p-type conducting properties of the as-prepared α-$BaCu_2S_2$ thin films further illustrates that such a thin film deposition technique is effective for high-performance devices.

Acknowledgment. Financial support from NSF of China (Grant 20471068) is acknowledged.

Supporting Information Available: Cross-sectional SEM image and electron diffraction pattern of the $BaCu_2S_2$ thin film (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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