Transparent *p*-type conducting $BaCu_2S_2$ films

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p-type conducting films of α-$BuCu_2S_2$ have been deposited onto glass and KBr substrates, yielding a conductivity of 17 S/cm and a Hall mobility of 3.5 $cm^2/V\,s$. For a 430-nm-thick film, the optical transparency approaches 90% in the visible portion of the spectrum at 650 nm, and a transparency of 40% extends throughout the infrared to the long-wavelength cutoff of the KBr substrate at 23 μm. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1485133]

Wide band-gap oxides such as tin-doped indium–oxide and aluminum-doped zinc–oxide are well known and widely used *n*-type transparent conductors. On the other hand, *p*-type materials with equivalent optical transparency and electrical conductivity are unknown, although efforts have recently been directed at the development of such materials on the basis of Cu compounds such as $CuAlO_2$,[1–4] $CuScO_{2+x}$,[5] $SrCu_2O_2$,[4] and LaCuOS.[6] In comparison with tin-doped indium–oxide and aluminum-doped zinc-oxide, however, these Cu-based materials exhibit much lower figures of merit with respect to their transparency and conductivity. Conductivity in these systems is limited, in part, by low hole mobilities, which have been reported to be $\leq 0.4\ cm^2/V\,s$. The rather low conductivity, 0.01 S/cm, reported for LaCuOS thin films is somewhat surprising in view of the higher covalency of the Cu–S interactions in this compound relative to the Cu–O interactions in the oxides; higher covalency is expected to lead to broader bands, smaller effective masses, hence, higher mobilities and smaller dopant ionization energies, both of which should result in improved conductivity.[7] To examine this covalency issue in more detail and to determine whether improved mobilities can be observed in thin films of complex Cu sulfides, we have studied the preparation and electrical properties of the compound $BaCu_2S_2$.

$BaCu_2S_2$ crystallizes in a low-temperature orthorhombic form (α)[8] and a high-temperature tetragonal form (β);[9] in this work, we focus on the low-temperature compound. The structure is characterized by a three-dimensional linkage of CuS_4 tetrahedra that encapsulates the Ba atom in a seven-coordinate site. The CuS_4 tetrahedra are connected by sharing both vertices and edges. Interestingly, edge sharing results in a one-dimensional chain of tetrahedra and a short Cu–Cu distance of 2.71 Å (Fig. 1). For comparison, the shortest Cu–Cu interaction in the delafossite $CuAlO_2$ is 2.86 Å.[10] Short interatomic distances are desirable for obtaining materials with improved conductivity, since shorter distances result in broader bands and their associated transport advantages.[7]

Thin films were deposited onto glass and KBr substrates by rf sputtering with a sintered-target disk and a gas mixture of Ar/He (60%/40%) at 35 mTorr and 80 sccm. The substrate was maintained at 573 K, and following deposition, the film was annealed in Ar at the same temperature for an additional 5 min. The 50-cm-diam target of $BaCu_2S_2$ was fabricated by pressing a powder at 4 tons and then annealing at 1048 K for 5 h in an Ar atmosphere. The powder was prepared by heating a mixture of the reagents $BaCO_3$ (Cerac, 99.9%) and Cu_2S (Cerac, 99.5%) at 923 K for 1 h under a flowing stream of H_2S(g) and then cooling to room temperature under flowing Ar(g). Phase identification was accomplished by using a Siemens D-5000 x-ray diffractometer; film thickness was established with an Alpha-Step 500 surface profiler; surface topography was examined with a NanoScope II atomic-force microscope; carrier type was established by using a hot probe in conjuction with a HP 3457A multimeter; and electrical measurements were performed on films deposited with a cross-shaped mask to improve the quality of the Hall data. A Filmetrics F20-VIS diode array was employed to determine the transmission of the films in the visible portion of the spectrum, and a Nicolet 510P Fourier transform infrared (FT-IR) spectrometer was used to determine transmission properties in the infrared.

As seen from the x-ray data in Fig. 2, the film adopts the low-temperature, α form of $BaCu_2S_2$; no diffraction lines attributable to the high-temperature form are evident in the pattern. From atomic-force microscope measurements, the surface of the film is found to be relatively smooth with a roughness of ± 20 nm. Electrical measurements reveal a *p*-type conductivity of 17 S/cm, a mobility of 3.5 $cm^2/V\,s$,

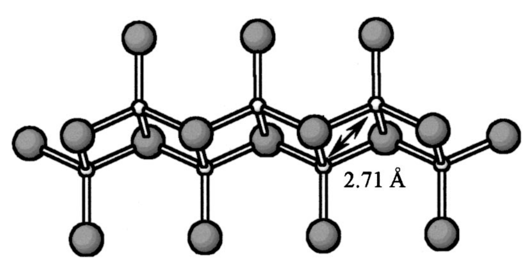

FIG. 1. Structure of one-dimensional copper–sulfide chains in α-$BaCu_2S_2$. Small circles represent Cu atoms, and large circles represent S atoms.

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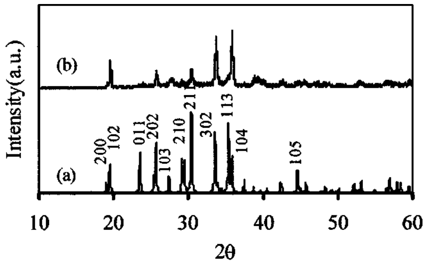

FIG. 2. (a) Calculated and (b) observed x-ray diffraction patterns of thin-film α-$BaCu_2S_2$.

and a carrier concentration of $10^{19}/cm^3$. The p-type conductivity is consistent with recent observations[11] of similar behavior in the α form of the powder, and the magnitude of the conductivity exceeds that reported for LaCuOS by a factor of 10^3. The mobility may be compared to values near 20 $cm^2/V\,s$ for a typical n-type transparent conductor such as indium–tin–oxide.[12]

As shown in Fig. 3, prior to the band edge near 540 nm, the film exhibits a transparency near 70% with a maximum of 90% at 650 nm. By using extrapolation methods[13] for direct and indirect character (Fig. 3,) the band gap is estimated to be 2.3 eV. Because the material can be processed at low temperatures, it can be directly deposited onto KBr substrates. For a 430-nm-thick film, a transmission near 40% extends to the long-wavelength cutoff of the substrate at 23 μm (see Fig. 4).

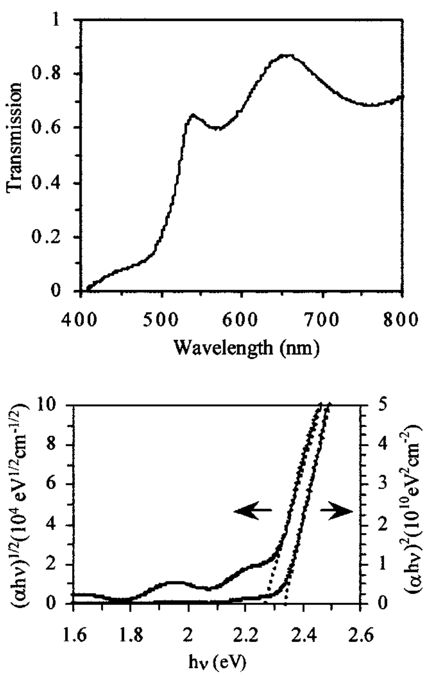

FIG. 3. (Top) Optical transmission spectrum of α-$BaCu_2S_2$ film in visible region. (Bottom) Estimate of band gap for indirect and direct character.

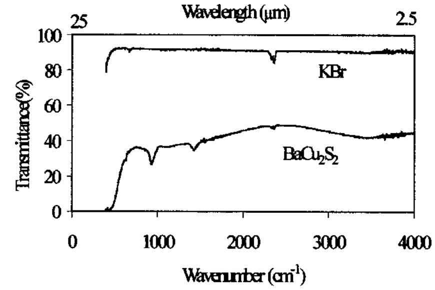

FIG. 4. Optical transmission spectrum of α-$BaCu_2S_2$ film in infrared region.

In summary, we have found that the low-temperature form of $BaCu_2S_2$ can readily be deposited in polycrystalline, thin-film form. A hole mobility of 3.5 $cm^2/V\,s$ and a conductivity of 17 S/cm have been measured for undoped material; higher conductivities should be attainable in appropriately doped samples. On the basis of other work performed in our lab, we believe that the limited conductivity of LaCuOS relative to $BaCu_2S_2$ may be related to defect formation associated with the high-temperature ($T=1073$ K) processing of LaCuOS that is required for its formation and crystallization. Of course, $BaCu_2S_2$ exhibits a smaller band gap than LaCuOS (3.1 eV,) but we have recently identified other complex p-type conducting Cu sulfides with band gaps near 3 eV which, like $BaCu_2S_2$, can be processed at relatively low temperatures ($T\sim673$ K).

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