Transparent *p*-type conducting $CuScO_{2+x}$ films

N. Duan and A. W. Sleight[a)]
Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

M. K. Jayaraj and J. Tate
Department of Physics, Oregon State University, Corvallis, Oregon 97331

(Received 8 May 2000; accepted for publication 29 June 2000)

Transparent films of $CuScO_{2+x}$ have been prepared which show *p*-type electrical conductivity. The temperature dependence of the conductivity indicates semiconducting behavior with an apparent room temperature activation energy of 0.11 eV. The highest room temperature conductivity observed was 30 S cm^{-1}. Films 110 nm thick show 40% transparency in most of the visible spectrum and become much more transparent in the infrared spectrum. The *p*-type behavior was confirmed by the Seebeck effect. © *2000 American Institute of Physics.* [S0003-6951(00)00535-0]

The best known transparent conductors such as doped ZnO, In_2O_3, or SnO_2 are *n*-type conductors. There has been considerable interest in finding *p*-type electrical conducting films that are transparent in the visible and/or infrared spectrum.[1] In this regard, $CuAlO_2$ has attracted recent attention.[2,3] Films of $CuAlO_2$ have shown transparency in the visible and infrared spectrum with electrical conductivities reported to be as high as 1 S cm^{-1} but generally in the range 0.1–0.5 S cm^{-1}.

$CuAO_2$ compounds isostructural (Fig. 1) with $CuAlO_2$ are known where A is Fe, Co, Rh, Ga, Sc, Y, or a lanthanide.[4] Intercalation with oxygen to form $CuAO_{2+x}$ phases is possible for the compounds with the larger A cations. Such an intercalation reaction is unknown for $CuAlO_2$, presumably because the small size of Al^{3+} shrinks the lattice to the point where oxygen cannot readily penetrate. Cava and co-workers[5,6] have investigated the properties of polycrystalline $CuYO_{2+x}$ and $CuLaO_{2+x}$ phases. After oxygen intercalation, a conductivity as high as 10 S cm^{-1} was observed. No films of $CuYO_{2+x}$, $CuLaO_{2+x}$, or $CuScO_{2+x}$ have been reported, and no electrical transport data have been reported for $CuScO_{2+x}$ phases.

Polycrystalline $CuScO_2$ was prepared from an intimate mixture of Cu_2O and Sc_2O_3. This mixture was pelleted and heated at 1100 °C for 24 h. X-ray diffraction of this product showed only $CuScO_2$. A 2 in. diam sputtering target was prepared by pressing and heating a pellet of $CuScO_2$ at 1100 °C for 12 h. Sputtering utilized on-axis geometry and a background argon pressure of 10 mTorr. The substrate was silicon or amorphous silica heated to 300 °C. The initially deposited film was amorphous by x-ray diffraction. Rapid thermal annealing of the film for 3 min at 700 °C under oxygen produced polycrystalline $Cu_2Sc_2O_5$. Further annealing at 900 °C under argon for 10 min produced a polycrystalline film of $CuScO_2$ that was electrically insulating and highly transparent, showing an optical band gap of 3.3 eV. Treating this film under oxygen at 450 °C for 2 h produced a polycrystalline $CuScO_{2+x}$ film. This 110 nm thick, light-brown film on a silica substrate showed 40% transparency in the visible spectrum (Fig. 2). A film on a silicon substrate is much more transparent in the infrared region as shown in the inset in Fig. 2. The feature at about 9 μm may be related to the apparent room temperature activation energy obtained from conductivity measurements. Four probe electrical conductivity measurements on this film over the temperature range 80–300 K showed semiconducting behavior. The log σ vs $1/T$ plot (inset in Fig. 3) is not well fit by a straight line.

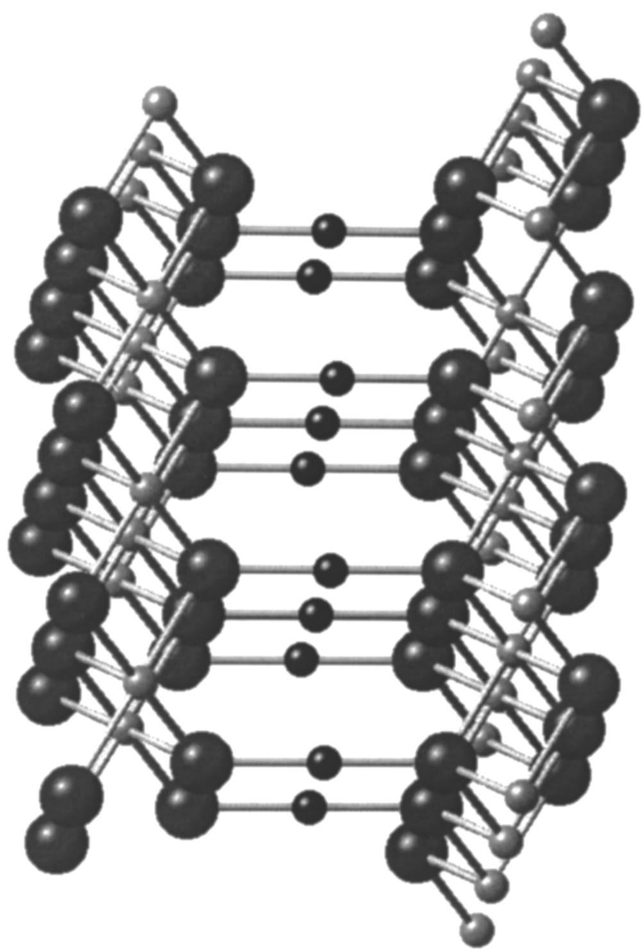

FIG. 1. Structure of $CuAO_2$ phases with Cu (small dark spheres) coordinated to two oxygen atoms (large dark spheres) and A (small light spheres) coordinated to six oxygen atoms.

[a)]Author to whom correspondence should be addressed; electronic mail: arthur.sleight@orst.edu

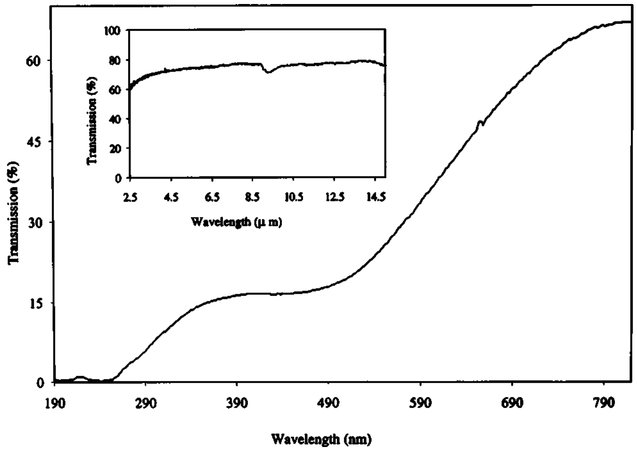

FIG. 2. Optical transmission spectrum for a 110 nm thick $CuScO_{2+x}$ film with infrared transmission in the inset.

However, the log σ vs $1/T^{1/4}$ plot is close to a straight line, suggesting a variable range hopping model is appropriate.[7] The activation energy derived from the slope in the Fig. 3 inset increases with increasing temperature becoming 0.11 eV at room temperature. The room temperature conductivity shown in Fig. 3 is about 15 S cm^{-1}; however, we have observed a room temperature conductivity as high as 30 S cm^{-1}

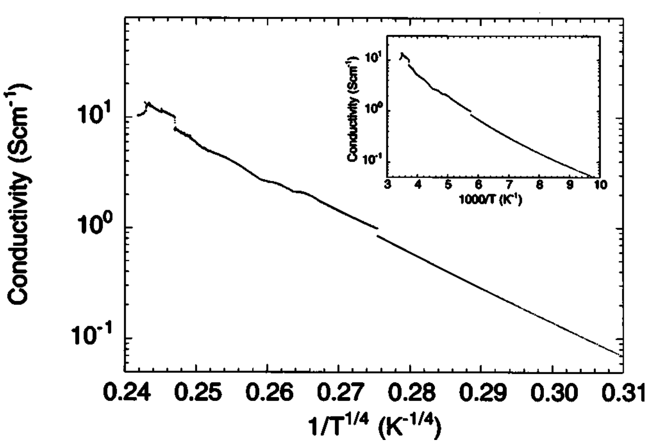

FIG. 3. Log conductivity vs $1/T^{1/4}$ and vs $1/T$ (inset) for a $CuScO_{2+x}$ film.

in $CuScO_{2+x}$ films. Thermopower measurements established the conductivity as *p*-type.

The holes produced in the valence band of $CuAO_{2+x}$ may be trapped as Cu^{2+} centers adjacent to an oxygen interstitial. If so, the optical absorption in the visible spectrum and the activated conductivity are presumably related to excitations to move the hole carrier away from the oxygen interstitial. Qualitatively, this trapping of the holes would contribute to their decreased mobility relative to that of *n*-type carriers, and substantially decrease the infrared absorption expected if the carriers were really free carriers as in the case of *n*-type conducting films.

The conductivities we have observed in *p*-type $CuScO_{2+x}$ are much higher than those reported for the *p*-type $CuAlO_2$ films. This is presumably due, at least in part, to the ease of increasing carrier concentration through oxygen intercalation. Oxygen annealing is necessary to induce conductivity in the films, and electron probe microanalysis confirms an increased oxygen content in doped $CuScO_{2+x}$ films that have become conducting as a result of such an annealing procedure. The conductivities of our films are still much lower than routinely found for *n*-type transparent conductors. However, with the great range of composition possible in the $CuAO_2$ family, further improvements in properties are likely.

The authors thank Andrew Draeseke for assistance, especially with the oxygen annealing. This research was supported by the National Science Foundation.

[1] G. Thomas, Nature (London) **389**, 907 (1997).
[2] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, Nature (London) **389**, 939 (1997).
[3] R. E. Stauber, J. D. Perkins, P. A. Parilla, and D. S. Ginley, Electrochem. Solid-State Lett. **2**, 654 (1999).
[4] R. D. Shannon, D. B. Rogers, and C. T. Prewitt, Inorg. Chem. **10**, 713 (1971).
[5] R. J. Cava, H. W. Zandbergen, A. P. Ramirez, H. Takagi, C. T. Chen, J. J. Krajewski, W. F. Peck, Jr., J. V. Waszczak, G. Meigs, R. S. Roth, and L. F. Schneemeyer, J. Solid State Chem. **104**, 437 (1993).
[6] R. J. Cava, W. F. Peck, Jr., J. J. Krajewski, S.-W. Cheong, and H. Y. Hwang, J. Mater. Res. **9**, 314 (1994).
[7] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).