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Hall mobility of cuprous oxide thin films deposited by reactive direct-current magnetron sputtering

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Cuprous oxide (Cu_2O) is a promising earth-abundant semiconductor for photovoltaic applications. We report Hall mobilities of polycrystalline Cu_2O thin films deposited by reactive dc magnetron sputtering. High substrate growth temperature enhances film grain structure and Hall mobility. Temperature-dependent Hall mobilities measured on these films are comparable to monocrystalline Cu_2O at temperatures above 250 K, reaching 62 $cm^2/V\,s$ at room temperature. At lower temperatures, the Hall mobility appears limited by carrier scattering from ionized centers. These observations indicate that sputtered Cu_2O films at high substrate growth temperature may be suitable for thin-film photovoltaic applications. © *2011 American Institute of Physics.*
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Cuprous oxide (Cu_2O), a compound semiconductor with a direct band gap of 1.9–2.1 eV,[1] is a promising material for thin-film photovoltaic applications due to its elemental abundance in the earth's crust[2] and nontoxicity. Although the Shockley–Queisser efficiency limit for Cu_2O is about 20%, the maximum efficiency realized using oxidized Cu metal foils is 2.01%.[3] This low record efficiency stems from a variety of factors that remain poorly understood in Cu_2O, including poor collection probability of photoexcited carriers, high surface recombination, and unoptimized device architecture. Additionally, to improve the prospects for this candidate solar cell material, it is desirable to synthesize Cu_2O thin films using standard manufacturing processes such as sputtering while retaining electron transport properties comparable to or surpassing monocrystalline material.

High-quality Cu_2O thin films have been deposited by various methods, such as sputtering,[4,5] pulsed laser deposition,[6] molecular beam epitaxy,[7] chemical vapor deposition,[8] and electrochemical deposition.[9] Among these deposition methods, reactive direct-current (dc) magnetron sputtering is a relatively cost-effective process that can be used for large-area device fabrication. In this study, we sputtered high-quality Cu_2O films that have sufficiently large grain size for thin-film photovoltaic applications. Additionally, we conducted temperature-dependent Hall effect measurements to identify the dominant mechanism limiting carrier mobility, and determined that Cu_2O films grown via sputtering exhibit majority carrier mobilities sufficiently high for thin-film photovoltaic applications.

Cu_2O thin films were deposited on GE-124 fused quartz glass substrates by reactive dc magnetron sputtering using an ATC-2200 (AJA International) in an argon and oxygen atmosphere. The substrate temperature was controlled using quartz lamps. A constant power (dc 50 W) was applied to a metallic copper target (2 in. diameter, 99.999% pure, Kurt J. Lesker Co.). The base and working pressures of the chamber were 1.3×10^{-5} Pa and 0.53 Pa, respectively. The phase purity of Cu_2O was controlled by varying the flow rate ratio of

argon and oxygen between 1:0.35 and 1:0.39. The average deposition rate was 3.4 nm/min.

For thin-film photovoltaic applications, columnar grain structure with a grain size larger than the film's thickness is desired.[10] To control morphology, the substrate temperature during film growth was varied. By adopting the Zone Model proposed by Movchan and Demchishin[11] for sputtered films, the temperatures were chosen to be 300 K ($0.2T_m$, where $T_m = 1508$ K is the Cu_2O melting temperature), 600 K ($0.4T_m$), and 1070 K ($0.7T_m$). These choices represent each regime proposed in the model. Film morphology was studied using a Zeiss ULTRA55 field-effect scanning electron microscope (SEM). The SEM micrographs in Fig. 1 show a change from fiberlike grains to columnar grains, as well as an increase in grain size, as the substrate temperature increases. Digital image processing was used to estimate average grain sizes as follows: 79 ± 17 nm, 228 ± 57 nm, and 884 ± 373 nm for the samples grown at 300 K, 600 K, and 1070 K, respectively.

The phase and crystal structure were characterized by x-ray diffraction (XRD) using PANalytical X'Pert Pro diffractometer with Cu-$K\alpha$ radiation. XRD confirmed that higher substrate temperature results in films with better crystallinity. As observed from the Bragg–Brentano scans in Fig. 2, the diffraction peaks of all samples are well matched to the reference pattern of Cu_2O and the peaks of other phases (e.g., Cu and CuO) were not detected. All samples also exhibited (200) out-of-plane preferred orientation. Samples
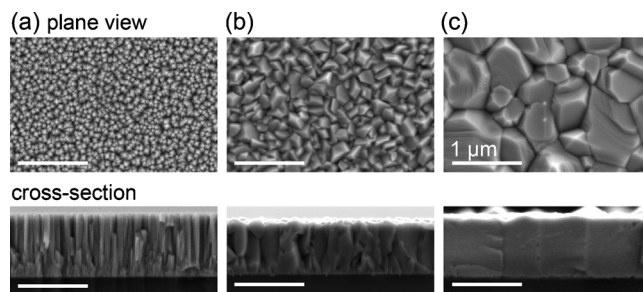

FIG. 1. SEM images of Cu_2O films with growth temperatures of (a) 300 K, (b) 600 K, and (c) 1070 K. All images to same scale; all size bars represent 1 μm.

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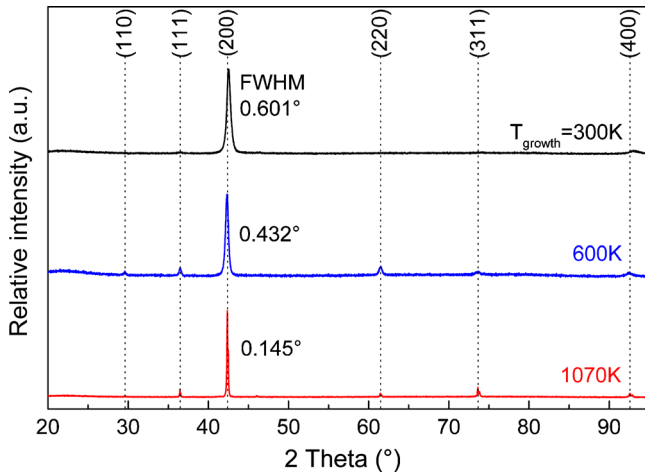[b]Electronic mail: buonassisi@mit.edu.

FIG. 2. (Color online) X-ray diffraction patterns of the samples with varying growth temperatures. The patterns are normalized to the same maximum height. Dotted lines represent the reference peaks of Cu_2O (ICDD PDF No. 01-071-3645).
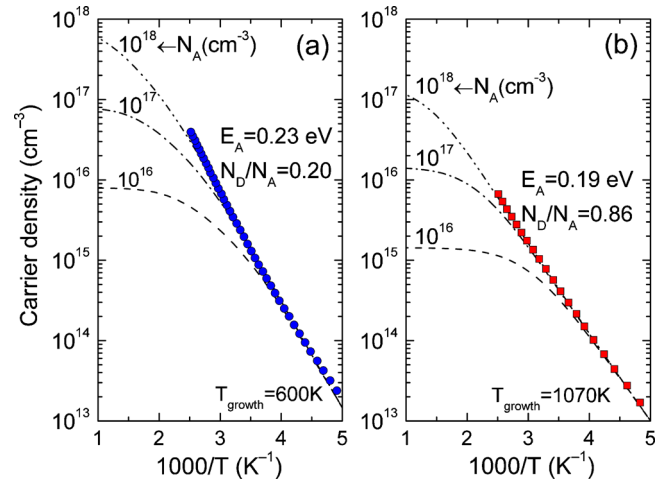

FIG. 3. (Color online) Temperature-dependent carrier density of Cu_2O films with growth temperatures (a) 600 K (blue circle) and (b) 1070 K (red square). Lines represent the exact solution from theoretical model with given acceptor density.

grown at higher substrate temperatures showed narrower diffraction peaks due to the increase in grain size. The smallest full-width at half maximum of the (200) peak was 0.145° with a substrate temperature of 1070 K.

We measured the temperature-dependent Hall effect using the van der Pauw configuration. Ohmic Au contacts were deposited on the corners of 1×1 cm^2 Cu_2O film samples using electron beam evaporation. Samples were placed in a closed-cycle He cryostat on a copper cold finger in a near-vacuum environment ($P < 0.1$ Pa); a resistive heater was used for temperature control. Measurement temperatures were kept below 400 K to prevent bulk phase change and persistent photoconductivity decay.[12] All samples exhibited p-type conductivity only and strong temperature dependence. We were unable to measure reproducible Hall voltages from the sample grown at 300 K due to its low mobility (<1 cm^2/V s); the remaining samples exhibited stable Hall voltages. Hall voltages V_H were measured using magnetic field $B = 0.65$ T and excitation current I. Carrier density p was calculated using the relationship $p = IB(edV_H)^{-1}$, where e is the electron charge, and d is the film thickness.

Figure 3 shows the temperature dependences of carrier density for samples grown at 600 and 1070 K. We fit the low temperature portion of the data using the low-temperature approximation[4,13] ($p \ll N_A - N_D$) for carrier density in a compensated semiconductor,

$$p = (2\pi m^* kT/h^2)^{3/2}[(N_A/N_D) - 1]\exp(-E_A/kT), \quad (1)$$

where the effective mass m^* can be taken as $0.58m_0$,[14] k is Boltzmann's constant, h is Planck's constant, N_A is the acceptor density, N_D is the donor density, and E_A is the activation energy. This model assumes only one type of singly charged acceptor is present, and that all donors are ionized ($N_D = N_{D^+}$). Using this model, we estimate E_A to be 0.23 eV and 0.19 eV for samples grown at 600 K and 1070 K, respectively. These activation energies are in the range of previously reported experimental values, between 0.16 and 0.42 eV.[4,15,16]

Fitting the low-temperature portion of our data with Eq. (1) provides estimates of both E_A and the compensation ratio (N_D/N_A). The fits yield the ratios of 0.20 and 0.86 for

samples grown at 600 K and 1070 K, respectively. We estimate the acceptor density using the exact form[17] of Eq. (1), which will saturate at high temperature when acceptors are completely ionized, and extending our fits to include all of our data. By calculating the net carrier density for various values of N_A (using the values of E_A and N_D/N_A provided by the low-temperature fits), we expect samples grown at 600 K and 1070 K to have acceptor densities of at least 2.2×10^{18} cm^{-3} and 2.7×10^{17} cm^{-3}, respectively. However, since the carrier densities of these samples did not saturate at the experiment's maximum temperature, these values represent lower bounds on the acceptor densities.

For the sample grown at 600 K, we observe a change in the slope in Fig. 3(a) as measurement temperature increases. This behavior cannot be fit using the single-acceptor model, and could be caused by multiple types of acceptors with different energy levels. Previous experimental work[18,19] and *ab initio* calculations[20,21] have both suggested the possibility of multiple acceptor levels. A substantially improved fit can be generated using a two-acceptor model, which provides acceptor level energies of 0.20 and 0.37 eV. Interestingly, the low energy acceptor level is close to the acceptor level (0.19 eV) of the sample grown at 1070 K. However, due to the number of parameters, we have less confidence in this fit. In addition, the lower bound on N_A provided by the two-acceptor model is consistent with the one-acceptor model; thus, we use the results from the one-acceptor model in the subsequent analysis for simplicity.

In Fig. 4, we compare the temperature-dependence of our samples' Hall mobilities to theoretical and experimental values of monocrystalline Cu_2O.[16,22–26] Shimada and Masumi[24] modeled the Hall mobility of Cu_2O when limited by longitudinal-optical (LO) phonon scattering with 220 and 960 K modes; the origin of the discrepancy between theoretical and experimental mobilities at temperatures above 200 K is currently unresolved. The Hall mobilities of both sputtered samples are comparable to that of monocrystalline Cu_2O at temperature above 250 K. The Hall mobility of the $T_{growth} = 1070$ K sample was 62 cm^2/V s at room temperature (293 K) and 43 cm^2/V s at a typical solar cell operating temperature of 60 °C (333 K).
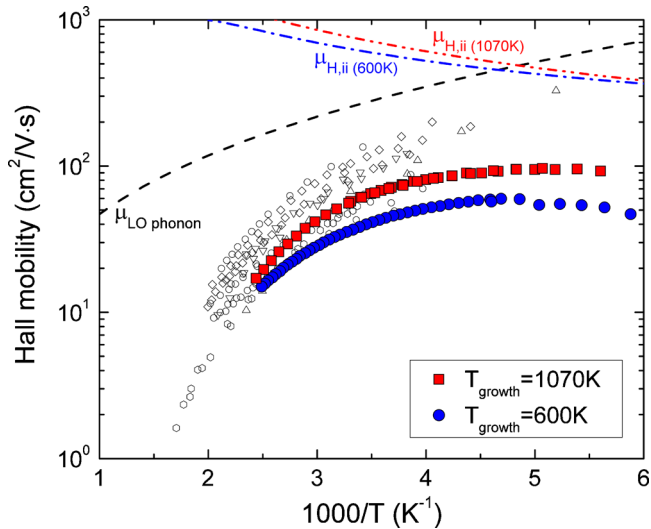
FIG. 4. (Color online) Temperature-dependent Hall mobility of Cu$_2$O films with growth temperature 600 K (blue circle) and 1070 K (red square). Open symbols represent monocrystalline Cu$_2$O from various references; Ref. 25 (triangle-up), Ref. 26 (triangle-down), Ref. 23 (hexagon), Ref. 22 (diamond), and Ref. 16 (circle). Lines represent theoretical limits by LO phonon scattering (Ref. 24) (black dash), ionized center scattering for the T_{growth}=600 K sample with N_A=2.2×10^{18} cm^{-3} (blue dashed-dotted), and for the T_{growth}=1070 K sample with N_A=2.7×10^{17} cm^{-3} (red dashed-dotted-dotted).

The mobilities of our samples appear to be limited by different factors than monocrystalline Cu$_2$O at temperatures below 250 K. Because our films exhibit higher carrier concentrations relative to monocrystalline Cu$_2$O, there will be a higher density of ionized centers, likely native defects. We calculate the ionized-impurity-limited mobility $\mu_{H,ii}$ using[27]

$$\mu_{H,ii} = r_{H,ii} \frac{128\sqrt{2\pi}(\varepsilon\varepsilon_0)^2(kT)^{3/2}}{\sqrt{m^*}N_iZ^2e^3}\left[\ln(1+b) - \frac{b}{1+b}\right]^{-1},$$

(2)

where $b=24m^*kT/\hbar^2\beta_s^2$, $r_{H,ii}$ is the Hall coefficient for ionized impurity scattering (equal to 1.93), ε is the relative dielectric constant of Cu$_2$O, ε_0 is the dielectric constant of vacuum, Z is the charge on the scattering center and β_s is the inverse screening length. For a p-type semiconductor compensated by singly charged donors, the ionized impurity density N_i is equal to $p+2N_{D^+}$. The estimated lower bounds of donor density were used to calculate the impurity density. Therefore, our calculation of μ_{ii} is actually an upper bound, and could be shifted downward in Fig. 4. Other factors for polycrystalline Cu$_2$O films such as scattering due to grain boundaries and dislocations were considered but they could not accurately model the measured Hall mobility. Thus, we conclude that the scattering from ionized centers is the likely limiting mechanism in these samples at lower temperatures.

In summary, we have shown that reactive dc magnetron sputtering at high substrate temperature can be used to deposit high-quality Cu$_2$O films suitable for thin-film photovol-

taic applications. Temperature-dependent Hall measurements reveal that the sputtered films exhibit high Hall mobility, comparable to that of monocrystalline Cu$_2$O at temperature above 250 K. Lastly, we deduce that the Hall mobility is limited by the scattering from ionized centers at low temperature.

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