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Nucleation and growth of Cu_2O in the reduction of CuO thin films

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The combination of $^{16}O(\alpha,\alpha)^{16}O$ oxygen resonance measurement and transmission electron microscopy (TEM) provides an effective method to study the kinetics of nucleation and growth of the Cu_2O phase during reduction of CuO thin films. The oxygen-loss kinetics in the CuO thin films upon vacuum annealing has been monitored with use of the oxygen resonance at 3.05 MeV. From the oxygen-loss measurement, the volume fraction of transformation of CuO to Cu_2O as a function of time and temperature has been determined. *In situ* TEM observation measures the growth of Cu_2O grains. When these results were analyzed with the model of phase transformation of Johnson, Mehl, and Avrami, the activation enthalpy of nucleation of the Cu_2O phase in the CuO matrix has been deduced as $\Delta E_n = 2.3$ eV/atom. The specific interfacial energy between the CuO and Cu_2O phases has been estimated to be in the range 0.3–0.85 eV/atom, and the number of atoms in the critical nucleus of Cu_2O has been calculated to be about 23 atoms.

Oxygen diffusion in oxides can lead to oxygen-concentration variation accompanied by a change in microstructure. During the reduction of CuO thin films, it was found that isolated and large Cu_2O grains emerge from the small CuO grain matrix. The discontinuous morphology of grain growth of Cu_2O in CuO is due to the migration of the Cu_2O-CuO phase boundary induced by oxygen outdiffusion along the moving phase boundary.[1] The unique morphological changes due to oxygen diffusion in copper oxide materials have been connected with diffusion-induced grain-boundary migration.[2,3] The grain growth of Cu_2O can be studied by using an electron microscope. However, the nucleation kinetics of the Cu_2O phase is not readily observed and quantified. Elastic nuclear resonance of $^{16}O(\alpha,\alpha)^{16}O$ near 3.05 MeV has the sensitivity of detecting a minute change in oxygen and offers an effective means of extending Rutherford backscattering technique (RBS) to the quantification of oxygen concentration in the oxide thin films.[4,5] By employing this technique, we measured the fractional volume change of the Cu_2O phase in the CuO matrix. Then, by using the Avrami equation,[6] we were able to analyze the nucleation kinetics of the Cu_2O phase during the reduction. From the analysis, we have deduced the activation enthalpy of nucleation and estimated the number of atoms in the critical nucleus and the interfacial energy between the CuO and Cu_2O phases during nucleation.

CuO thin films were prepared by reactive cathodic sputtering of Cu in oxygen atmosphere onto Si(100) substrates and SiO_2-thin-layer-covered NaCl substrates, followed by an annealing at 300 °C for 30 min in ambient oxygen. The base pressure in the sputtering chamber was 2×10^{-7} Torr. RBS was employed to measure the film thickness at 70 nm and the composition of the CuO film. Self-supporting CuO films were floated off the NaCl substrates and were placed on grids for observation in a transmission electron microscope. A hot stage was used in the electron microscope for *in situ* annealing. The CuO thin films on Si(100) substrates were isothermally annealed at temperatures from 375 to 550 °C in a quartz tube furnace with a vacuum level of 2×10^{-7} Torr. A Tandetron accelerator with a 1.7-MV terminal was used to conduct $^{16}O(\alpha,\alpha)^{16}O$ scattering resonance measurements for quantifying the oxygen concentration of the copper oxide film on the Si substrate.

Figure 1 shows bright-field images of the CuO thin-film sample before and after *in situ* annealing in the electron microscope. The initial grains which are identified as the pure CuO phase are randomly oriented with a mean grain size of 15 nm. After an annealing to 550 °C, grain growth occurs as a function of time 15, 30, and 45 min corresponding respectively to the bright field images in Figs. 1(b), 1(c), and 1(d). By examining the selective diffraction patterns of the isolated and large grains which are randomly distributed in the fine grain matrix, we have determined these larger grains to be Cu_2O grains.

CuO thin films on a Si(100) substrate were also isothermally annealed in vacuum at different temperatures. $^{16}O(\alpha,\alpha)^{16}O$ resonance has been employed to measure the oxygen concentration change during the reduction of the CuO thin film sample. Figure 2 shows the oxygen variation near the surface of the CuO sample measured at 3.05 MeV as a function of time at 550 °C. The inset in Fig. 2 exhibits the Cu signal and resonant oxygen signal corresponding to the pure CuO (the broken curve) and pure Cu_2O (the solid curve) phases observed by RBS at 3.05 MeV. By subtracting the Si background, the oxygen peaks in Fig. 2 have been simulated as $x=0.82$, 0.72, 0.58, and 0.52 in the form of CuO_x corresponding to the 15, 30, 45, and 60 min annealings at 550 °C. The oxygen concentration in the annealed copper oxide thin films

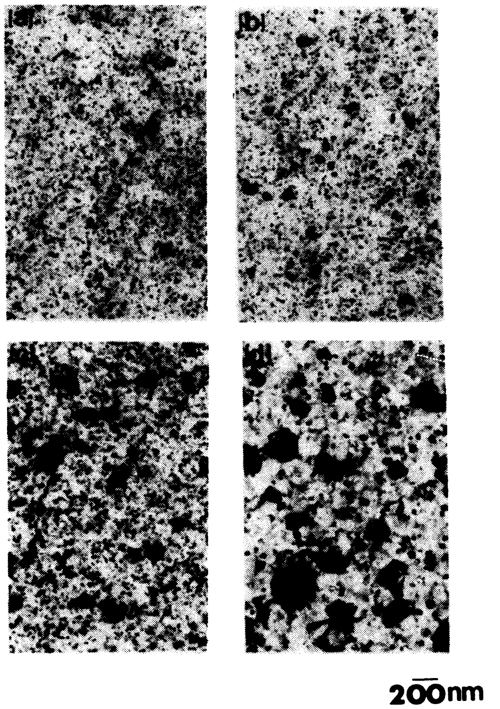

FIG. 1. Bright-field images of Cu_2O grains in the CuO matrix formed at 550 °C for different annealing times. Annealing was performed *in situ* in the TEM hot stage. (a) as-prepared CuO thin film; (b) 15 min; (c) 30 min; and (d) 45 min.

versus annealing time has been plotted in Fig. 3(a), indicating the oxygen loss rates at temperatures ranging from 375 to 550 °C during reduction.

The oxygen concentration in the form of CuO_x is related to the fraction X_t of transformation by

$$[CuO_x]_O = X_t[Cu_2O]_O + (1-X_t)[CuO]_O \ . \tag{1}$$

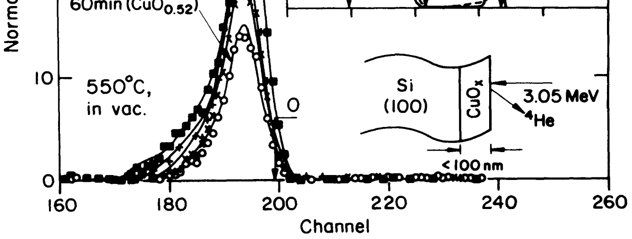

FIG. 2. RBS oxygen resonance spectra at different annealing times for a CuO thin film on Si(100) substrate after vacuum annealing at 550 °C. The computer simulated spectra (solid lines) are shown for comparison. The oxygen resonance peaks are subtracted from the Si background.

It shows that knowing the oxygen concentration x, the fraction X_t can be deduced. Here, we have ignored the contribution of free oxygen since the solubility of oxygen in the oxides and the compositional deviation from oxide stoichiometry are quite small.[7] Based on the oxygen resonance measurements of the oxygen concentration change near the surface of the cooper oxide sample as shown in Fig. 3(a), we plot the fraction of the transformed Cu_2O phase versus the annealing time at different temperatures in Fig. 3(b).

To describe the nucleation and growth of Cu_2O, we make the classical analysis of phase transformations of Johnson, Mehl, and Avrami.[6] Two assumptions for applying the Avrami equation are (1) the nucleation of Cu_2O phase is random and the rate is constant and (2) the growth is isotropic and linear with time. From Fig. 1(b) we observe that there is a small number of Cu_2O grains nucleated randomly. They are random in space; however, they are assumed to be constant in time. The size and the number of grains increase with annealing time. The estimation of nucleation rate by counting the numbers of Cu_2O nuclei in the bright field images is not readily achieved. The difficulty is that the Cu_2O nucleus cannot be identified until its grain size is beyond 30 nm in the early stage of nucleation. A linear growth of the Cu_2O

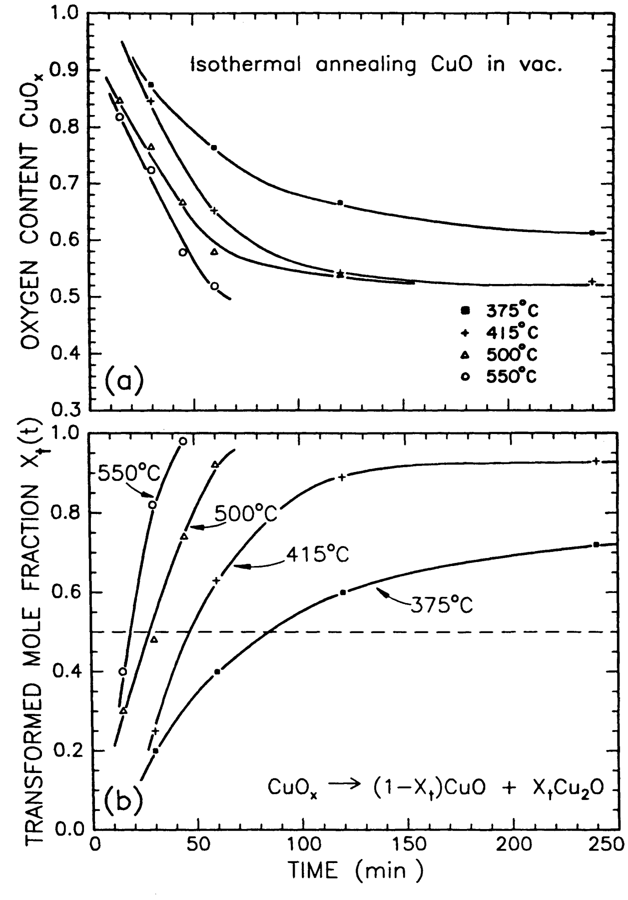

FIG. 3. (a) oxygen content in the copper oxide thin films vs annealing time upon isothermal annealing from 375 to 555 °C in vacuum. (b) The transformed mole fraction of the Cu_2O phase vs annealing time corresponding to (a).

phase has been observed.[1] By measuring the mean grain-boundary migration velocity versus the reciprocal temperature, the activation enthalpy of growth of Cu_2O can be estimated as $\Delta E_g = 1.1$ eV [see Fig. 4(a)].

The extended volume fraction X_{ext} of Cu_2O, which includes impingements and phantom nucleation, is related to the actual transformed volume fraction X_t by using the Avrami equation:

$$X_t = 1 - \exp(-X_{ext}) \ . \tag{2}$$

Since we have found that the Cu_2O grains can grow up to 250 nm in diameter, more than three times larger than the film thickness, we treat the transformation as a two-dimensional process. Based on the two assumptions mentioned above, we can express X_{ext} as

$$X_{ext} = \int_{\tau=0}^{\tau=t} \pi I G^2 (t-\tau)^2 d\tau = \frac{\pi I G^2 t^3}{3} \ . \tag{3}$$

Here, I and G stand for the nucleation and growth rates, which have been assumed to follow Boltzmann's distribution:

$$I = I_0 \exp(-\Delta E_n / kT) \ , \tag{4}$$

$$G = G_0 \exp(-\Delta E_g / kT) \ . \tag{5}$$

ΔE_n and ΔE_g are the activation enthalpies of nucleation and growth, respectively. By combining Eqs. (2) and (3) and taking a logarithm at a constant value of $X_t = 0.5$ $(t = \tau)$, we have

$$-\frac{\Delta E_n + 2\Delta E_g}{kT} + 3\ln\tau = \text{const} \ . \tag{6}$$

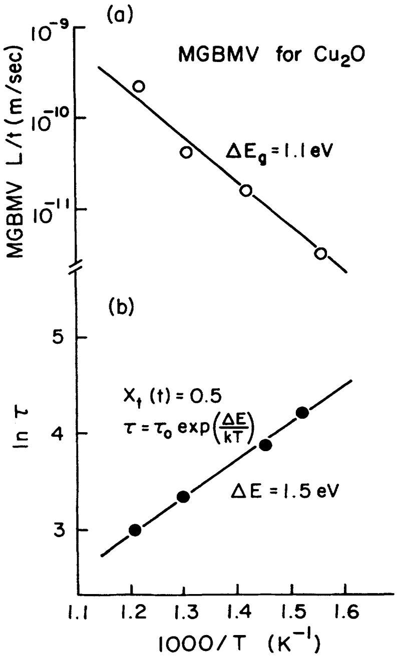

FIG. 4. (a) Mean grain-boundary migration velocity for Cu_2O grains vs reciprocal temperature. The activation enthalpy of growth has been obtained. (b) Logarithm of time required to transform $\frac{1}{2}$ of the CuO film into the Cu_2O phase as a function of $1/kT$.

In Fig. 3(b), we draw a horizontal line at $X_t = 0.5$ to interpret the four annealing curves so that the corresponding annealing times for the curves can be decided from the horizontal axis. The relation between time τ and temperature T can be obtained from the Arrhenius relation given by

$$\tau = \tau_0 \exp(\Delta E / kT) \ . \tag{7}$$

Figure 4(b) shows the results obtained and the activation energy of transforming CuO to Cu_2O is found to be

$$\Delta E = (\Delta E_n + 2\,\Delta E_g)/3 = 1.5 \text{ eV} \ . \tag{8}$$

We note that activation energy of overall reaction (ΔE) of CuO to Cu_2O and the activation enthalpy of growth of Cu_2O have been obtained by using $^{16}O(\alpha,\alpha)^{16}O$ resonance measurement and electron microscopy, respectively. From Eq. (8) we deduce the activation enthalpy of nucleation of Cu_2O, $\Delta E_n = 2.3$ eV. By knowing ΔE_n of the Cu_2O phase, we can estimate the number of atoms in the critical nucleus and the interfacial energy between CuO and Cu_2O by using classical nucleation theory.[8,9] To form a nucleus of N atoms, the energy change ΔE_n is

$$\Delta E_n = -N\,\Delta E_h + bN^{2/3}\gamma_{int} \ , \tag{9}$$

where ΔE_h and γ_{int} are the heat of phase transformation per atom and interfacial energy per atom between the CuO and Cu_2O phases, respectively, and b is a geometrical constant. For the critical nucleus, we obtain

$$N_{crit} = 2\,\Delta E_n / \Delta E_h = 23 \text{ atoms} \ , \tag{10}$$

$$b\gamma_{int} = (27/4)^{1/3} \Delta E_n^{1/3} \Delta E_h^{2/3} = 0.85 \text{ eV/atom} \ , \tag{11}$$

where N_{crit} is the number of atoms in the critical nucleus, and ΔE_h has been measured by differential scanning calorimetry to be 0.2 eV/atom.[10] The nucleation of Cu_2O in a CuO matrix is heterogeneous and random. For example, the heterogeneous nucleation may prefer the triple junctions of grain boundaries of CuO grains. The interfacial energy is an average of phase boundary energies between the CuO and Cu_2O phases and free surface of Cu_2O.

From the point of view of interfacial energy, it is favorable for a nucleus or a newly formed phase to be surrounded by low-energy coherent interfaces. In general coherent interfacial energies range from 0.001 to 0.1 eV/atom.[11] There are, however, no good matching planes between the CuO (monoclinic structure) and Cu_2O (cubic structure). The Cu_2O phase must consequently be bounded by high-energy incoherent interfaces, and so heterogeneous nucleation is favorable. In Eq. (11) the geometrical constant b varies from 1 to 3, where the last numerical value is estimated from the number of atoms in the critical nucleus.[12] Hence the range of γ_{int} varies from 0.3 to 0.85 eV/atom.

The error of the estimate of the critical nucleus and the interfacial energy is directly related to the vicinity of the two-dimensional model based on the Avrami equation and classical nucleation theory. The nucleation rate of the Cu_2O phase may not be constant all the time after the transient period, e.g., the nucleation rate may slow down in the later stage of the transformation when the grain size of the Cu_2O phase is larger than the film thickness. In our experiment, the mode parameter n, which is related to the mechanism of nucleation and growth morphology in the CuO-Cu_2O system, has been determined from the plot $\ln\ln[1-X_T(t)]^{-1}$ vs $\ln(t)$). The value of n was found to be around 2.5, which is less than 3 for the ideal two-dimension case. Also, it is worthwhile pointing out that the in-depth oxygen concentration is quite uniform within the thickness of 100 nm based on the oxygen depth profiling.[5]

In summary, we have employed the $^{16}O(\alpha,\alpha)^{16}O$ resonance to monitor the oxygen-loss kinetics during the reduction of CuO thin films. Combining the oxygen-loss measurement with transmission-electron-microscopy observation of Cu_2O grain growth, we have deduced an activation enthalpy of nucleation of the Cu_2O phase of $\Delta E_n=2.3$ eV. The specific interfacial energy between the CuO and Cu_2O phases has been estimated to be in the range of 0.3–0.84 eV/atom, and the number of atoms in the critical nucleus to be 23 atoms, on the basis of classical nucleation theory.

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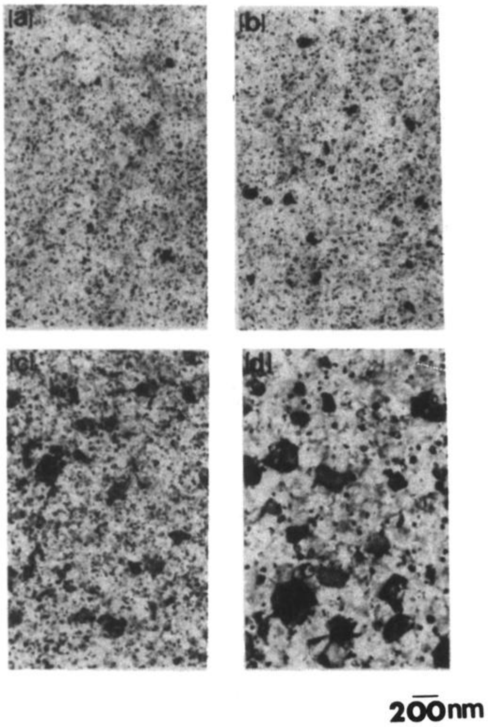

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