Coupling effect of the electric and temperature fields on the growth of nanocrystalline copper films

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(Received 15 November 2009; revised manuscript received 11 February 2010; published 23 March 2010)

The effect of an external static electric field on the grain growth in nanocrystalline Cu films was studied at different annealing temperatures. Transmission electron microscopy and x-ray diffraction indicate that the grain growth in Cu films is accelerated with various rates by an external electric field at different annealing temperatures. It is found that there is a coupling effect from the external electric and temperature fields on grain growth in Cu films during annealing. The growth rate is accelerated proportional to a factor $f(E)\cdot\mu^{T/100\,^{\circ}\mathrm{C}}$, which is determined from the theoretical derivation. The analysis indicates that the enhanced grain growth is achieved by the effect of the electric field on the vacancies migration and dislocation climb along grain boundaries.

DOI: 10.1103/PhysRevB.81.113405   PACS number(s): 61.82.Rx, 81.05.Bx, 65.80.−g, 61.72.Lk

With the continuous down scaling of the size of integrated circuits (ICs), guaranteeing the reliability of microelectronic devices becomes a major challenge for semiconductor technology in the future.[1,2] Copper has a lower electrical resistivity and less electromigration than aluminum and has therefore become the dominant on-chip interconnect material in IC.[3,4] The use of copper enhances the working speed and reduces the interconnect resistance-capacitance delay.[5] The microstructure of Cu films, such as grain size and texture, can impact on the resistance to stress-induced migration and electromigration in Cu interconnects remarkably.[6,7] Generally, Cu lines with a bamboolike grain structure offer the significant advantage of antielectromigration and those with (100) texture have a higher resistance to stress-induced migration compared to those with (111) texture.[8] Especially in fast IC, the working temperatures can be quite elevated and similar holds for the electric fields that accompany small distances close to sharp features inside modern IC.[9,10] Moreover, special applications, as, for example, in certain sensors, often lead to high temperatures and high electric fields. These can change the microstructure of Cu lines[11] and will finally lead to the degeneration of the microelectronic devices. Thus, it is important to know how the microstructure of Cu films evolves in different conditions.

It is well known that the growth of the grain size of nanoscale Cu films increases rapidly along with the annealing temperature. In addition to the temperature, it is also found that the electric field can influence the grain growth of metals.[12,13] However, it is still under debate whether external electric fields can accelerate grain growth or not. Jung and Conrad[14] found that the electric field could retard grain growth of electrodeposited Cu foil during annealing. However, Liu *et al.*[15] reported that the grain growth rate of Cu was accelerated by the field. Accelerated growth of the texture of cold-rolled steel under an applied electric field was also observed by He *et al.*[16] Consequently, the effect of the electric field on grain growth of Cu at different temperatures needs to be studied further. Especially interesting is the interdependence between electric field and temperature.

The purpose of the present Brief Report is to obtain the information about the effect of the external electric field on the grain growth of Cu films. Of specific interest is the coupling effect of the electric and temperature fields on grain growth. Furthermore, the intrinsic mechanism for grain growth influenced by the coupling effect is also discussed in detail.

The nanocrystalline (NC) Cu films were prepared by dc magnetron sputtering. Before deposition, all Si (111) substrates were cleaned ultrasonically in alcohol and then acetone for 20 min. Amorphous Ta films of about 10 nm thickness were first deposited onto the substrate under pure argon gas using a 99.95% purity Ta target. Then, without breaking the vacuum, 300-nm-thick Cu films were deposited on the amorphous Ta films. The base pressure was kept at about 6.5×10^{-5} Pa. During deposition, the chamber was filled with 99.999% Ar at a rate of 20 SCCM (SCCM denotes cubic centimeter per minute at STP), and the working pressure was 1.4 Pa. The sputtering powers of Ta and Cu were about 150 W and 70 W, respectively. The detailed preparation conditions of these films were reported previously.[17,18] The as-deposited samples were annealed for 30 min at different temperatures ranging from 300 to 500 °C with and without a 3 kV/cm electric field orthogonal to the Cu surface. The pressure during annealing was always maintained lower than 4.0×10^{-4} Pa, in order to avoid extensive oxidation of the Cu films. The schematic of the setup is presented in Fig. 1. The specimens were connected to the anode. The structure and grain size of the annealed Cu films were characterized by x-ray diffraction (XRD) with Cu $K\alpha$ radiation source and

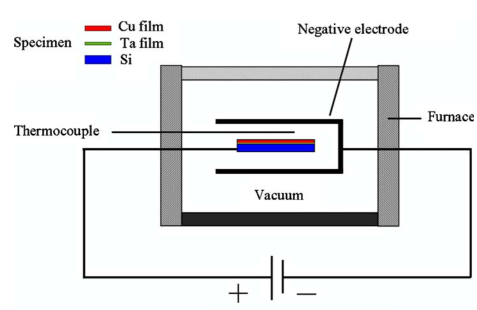

FIG. 1. (Color online) Experimental arrangement for electric and thermal treatment.

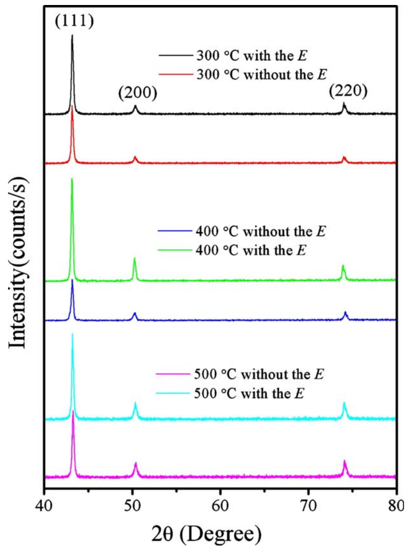

FIG. 2. (Color online) XRD patterns of the Cu films annealed at different temperatures with or without electric field.

transmission electron microscopy (TEM) (JEM-2100).

Figure 2 shows the XRD patterns of Cu films annealed at different temperatures with and without the electric field. It is found that all Cu films exhibited (111) preferentially oriented texture. The (111) preferential orientation is a prevalent characteristic of Cu films prepared by magnetron sputtering.[19] The electric field did not change the grain orientation. The grain size of annealed Cu films was determined by means of the Scherrer formula,[20] and the calculated values are in good agreement with the TEM results. Figure 3(a) presents the TEM picture of a Cu film annealed at 400 °C without electric field. The selected-area electron diffraction (SAED) ring pattern is shown in the inset of Fig. 3(a). Microstructure studies reveal that the degree of abnormal grain growth is very limited. Figure 3(b) presents a histogram of the grain-

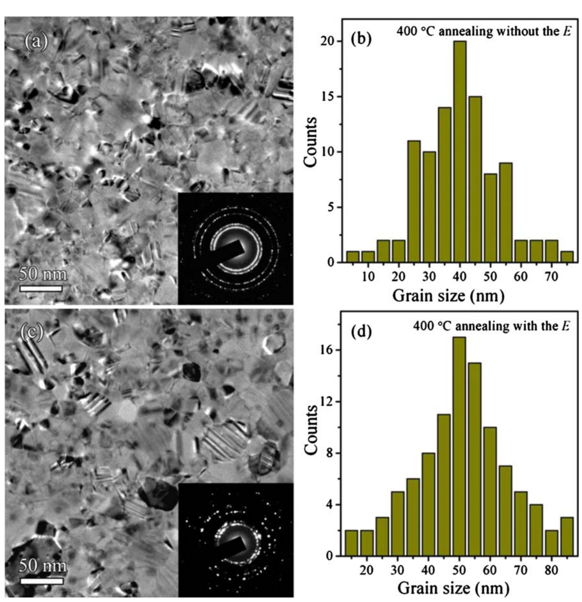

FIG. 3. (Color online) TEM micrographs of the Cu films annealed at 400 °C (a) with and (c) without electric field, and their corresponding grain-size distributions of the Cu films (b) and (d).

TABLE I. The grain size of Cu films annealed at different temperatures with and without electric field and their rate of change χ.

Temperature (°C)	300	400	500
D_T (annealing without electric field)	38.5	42.4	53.7
D_E (annealing with electric field)	39.8	50.4	112.3
The rate of change (χ) (%)	3.3	18.9	109.1

size distribution. The average grain size of the Cu film annealed without field is calculated to be ~42.4 nm. Figure 3(c) presents the top surface of the Cu film annealed at 400 °C with applied electric field and its SAED pattern. The grain size is clearly larger than that of the Cu film annealed without the electric field. The SAED rings in Fig. 3(c) are more discontinuous than in Fig. 3(a) since fewer grains reside in the selected area, which again confirms the larger size of the grains. A typical grain-size distribution for Cu films annealed under an applied electric field is shown in Fig. 3(d). The average grain size is ~50.4 nm, which is larger than that of Cu films annealed without the electric field. This finding indicates that the electric field accelerated the grain growth during annealing at 400 °C. The average grain size of Cu films annealed at different temperatures with and without the electric field is listed in Table I. The average grain size becomes larger when annealed under the electric field. The rate of changes (χ) is defined as follows:

$$\chi(T) = \frac{D_E - D_T}{D_T}, \qquad (1)$$

where D_E is the grain size after annealing inside the electric field E, D_T is the grain size without the electric field, and T is the annealing temperature. Table I shows that the χ increases from 3.3% to 109.1% when increasing the annealing temperature from 300 to 500 °C at the same electric field of 3 kV/cm. This suggests that the effect of the electric field on grain growth becomes stronger with the increase in annealing temperature. Here, the coupling effect is defined as the promoted effect of electric field on grain growth through the enhanced temperature.

According to the analysis for the χ of grain size listed in Table I, it is found that the χ increases about sixfold with each 100 °C increase under the applied electric field of 3 kV/cm. The change in χ with annealing temperature is shown as follows:

$$\chi(400\ ^\circ\mathrm{C})/\chi(300\ ^\circ\mathrm{C}) = 18.9\%/3.3\% = 5.72, \qquad (2a)$$

$$\chi(500\ ^\circ\mathrm{C})/\chi(400\ ^\circ\mathrm{C}) = 109.1\%/18.9\% = 5.77. \qquad (2b)$$

The numerical value μ of Eq. (2a) is approximately equal to that of Eq. (2b). The μ and T are related as follows:

$$\chi(T + 100\ ^\circ\mathrm{C}) = \mu \cdot \chi(T). \qquad (3)$$

Here, $\chi(T)$ is an exponential function of T. Given exponential function follows the expression:

$$\chi(T) = a \cdot b^{cT}, \qquad (4a)$$

$$\chi(T + 100\ ^\circ\mathrm{C}) = a \cdot b^{cT} \cdot b^{(100\ ^\circ\mathrm{C})c}, \qquad (4b)$$

where a, b, and c are all constants. One obtains from Eq. (3), Eqs. (4a) and (4b)

$$b^c = \sqrt[100\ ^\circ\mathrm{C}]{\mu}. \quad (5)$$

Considering Eqs. (4a) and (5), one obtains

$$\chi(T) = a \cdot \sqrt[100\ ^\circ\mathrm{C}]{\mu^T} = a \cdot \mu^{T/100\ ^\circ\mathrm{C}}. \quad (6)$$

Equation (6) reflects the relationship between the χ of grain size and the annealing temperature T.

Generally, the change in grain size of Cu films with annealing time will follow as:[21]

$$D_t^n - D_0^n = Kt = A_0 \exp(-Q/RT)t, \quad (7)$$

where D_0 is the initial grain size, D_t is the grain size at annealing time t, n is the grain growth exponent, A_0 is the pre-exponential, Q is the activation energy, and R is the gas constant. For the present $D_t^n \gg D_0^n$, the influence of D_0 is ignored. Thus, Eq. (7) reduces to[14]

$$D_t = A_0^{1/n} \exp(-Q/nRT)t^{1/n}. \quad (8)$$

From Eqs. (1) and (8), one obtains

$$\chi(T) = \frac{A_E^{1/n} \exp(-Q_E/nRT)t^n - A_0^{1/n} \exp(-Q_0/nRT)t^n}{A_0^{1/n} \exp(-Q_0/nRT)t^n}. \quad (9)$$

The $\chi(T)$ is given by

$$\chi(T) = \frac{A_E^{1/n} \exp[(Q_0 - Q_E)/nRT] - A_0^{1/n}}{A_0^{1/n}}, \quad (10)$$

where Q_0 and Q_E are the activation energies of grain growth with and without the applied electric field. Considering Eqs. (6) and (10), one can obtain

$$A_E^{1/n} = A_0^{1/n}[1 + a \cdot \mu^{T/100\ ^\circ\mathrm{C}}]\exp[(Q_E - Q_0)/nRT], \quad (11)$$

where A_0 is a constant. The $A_0^{1/n} \cdot a \cdot \mu^{T/100\ ^\circ\mathrm{C}}$ is affected by the electric field during annealing. When $E=0$, the $A_0^{1/n} \cdot a \cdot \mu^{T/100\ ^\circ\mathrm{C}}$ is zero, i.e., $a=f(E=0)=0$. Thus, Eq. (11) can be expressed by

$$A_E^{1/n} = A_0^{1/n}[1 + f(E) \cdot \mu^{T/100\ ^\circ\mathrm{C}}]\exp[(Q_E - Q_0)/nRT] \quad (12)$$

and the evolution of the grain size of the Cu films upon annealing in the electric field is given by

$$D_E = A_0^{1/n}[1 + f(E) \cdot \mu^{T/100\ ^\circ\mathrm{C}}]\exp[(Q_E - 2Q_0)/nRT]t^{1/n}, \quad (13)$$

where $f(E)$ is the function of E and $f(E=0)=0$, $\mu=5.77$. It can be found that the Q is affected by the electric field. The coupling factor $f(E) \cdot \mu^{T/100\ ^\circ\mathrm{C}}$ of the electric and temperature fields has a stimulating effect on the grain growth of Cu films, which acts in the Eq. (12) as the combined action of both the electric and temperature fields.

A normal grain growth is found for all Cu films, where the grain growth exponent n is ~ 2.[22,23] The relationship of $\ln[(D_t^2 - D_0^2)/t]$ and $1/T$ can be obtained from Eq. (7), as shown in Fig. 4. It is found that the Q_E and Q_0 are 74.5 kJ/mole and 38.7 kJ/mole, respectively. This indicates that the activation energy is enhanced by the action of the electric field. The previous research by Jung and Conrad[14] suggests that the external electric field only reduced the A_0, but no clear effect on the Q of grain growth. However, Li and Conrad[24] also reported that the electric field increased the Q by 20 kJ/mole for the Zn-5 wt. % Al alloy. From Eq. (8), it can be seen that the D decreases with the increased Q. Schwensfeir and Elbaum[25] also showed that the electric field increased grain boundary (GB) mobility in NaCl. Therefore, the coupling factor $f(E) \cdot \mu^{T/100\ ^\circ\mathrm{C}}$ is responsible for the accelerating grain growth induced by the electric field. The driving force of the grain growth becomes larger due to the coupling. It is noted that both present Q_E and Q_0 values are lower than the activation energy of electrodeposited NC Cu bulk (about 86 kJ/mol).[26] Notwithstanding, they are close to that of the GB diffusion for Cu, about 38–66 kJ/mol.[27,28] Consequently, the GB diffusion and migration can be thought of as the dominant growth mechanism.

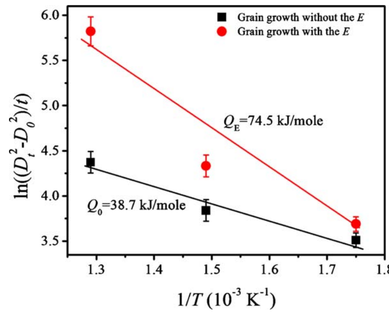

FIG. 4. (Color online) The activation energy of grain growth with and without electric field is determined from the slope of $\ln[(D_t^2 - D_0^2)/t]$ vs $1/T$.

The GB migration velocity V in metal is given by classical grain-growth theory as follows:[29]

$$V = dD/dt = MP, \quad (14)$$

where M is the GB mobility and P is the driving force. The latter is made up of two components for a pure metal

$$P = P_\mathrm{S} + P_\mathrm{GB}, \quad (15)$$

where P_S and P_GB are the volume-stored energy and GB energy, respectively. The P_S is mainly determined by the dislocation density in the interior of grains. For the P_GB, the dislocations and vacancies are often the major sources of GB energy, since GB consists of dislocations and vacancies.[30] Consequently, the density of dislocations and vacancies will directly determine the total driving force of grain growth.

Until now, the intrinsic mechanism for the effect of electric field on grain growth is still not fully understood,[14,15] since the electric field is different from the temperature and stress fields. The electron theory of metals considers that the vacancy is electronegative, and the lattice defect energy is a static electrical energy caused by a thin layer made of negative charge shielding against positive charge.[31] The charged surface induced by the electric field affects the migration of the vacancy, dislocation or boundary during annealing due to the perturbation of the electric state at the defects.[15] The increasing migration rate of the vacancies and dislocations via GB is thought to accelerate grain growth. For the present study, the coupling factor $f(E) \cdot \mu^{T/100\ ^\circ\mathrm{C}}$ of the electric and temperature fields was found, which is responsible for the accelerating grain growth. First, the electric field can produce an excess of vacancies.[13] Second, it was reported by Baranov that the development of the dislocation structure and density is accelerated by the electric field, which is responsible for the increasing flow stress of metal.[32,33]

For the present Si/Cu structure, the thermal stress will be developed during annealing due to the different thermal-expansion coefficients of Cu films and Si substrate. The variation in thermal stress in Cu films can be expressed as[34]

$$\Delta\sigma = \left(\frac{E_f}{1-\nu_f}\right)(\Delta\alpha)(\Delta T), \tag{16}$$

where $\Delta\sigma$ is the variation in thermal stress, E_f and ν_f are the elastic modulus and Poisson's ratio of the film, respectively, $\Delta\alpha$ is the thermal-expansion coefficient difference between Cu and Si ($\alpha_{Cu}=17.2\times10^{-6}\ °C^{-1}$, $\alpha_{Si}=3.0\times10^{-6}\ °C^{-1}$),[35] ΔT is the temperature deviation from a zero-stress status. The E_f of Cu films is determined to be 100 GPa by nanoindentation in our previous work,[17] while the ν_f obtained from the conventional coarse grain Cu is 0.33. The thermal stress in Cu films annealed at 400 °C is calculated to be ~420 MPa given the zero-stress status at 200 °C. As the annealing temperature is increased to 500 °C, the thermal stress will reach ~640 MPa. In our previous work,[17] for the submicron-thick Cu films with grain size ranging from 16 to 80 nm prepared by the same method and under the same conditions, their yield strengths vary from ~900 to ~550 MPa. In particular, the yield strength of a 300-nm-thick Cu film is ~800 MPa, which is close to the stress of the present Cu films. Moreover, other reports[36–38] show that the yield strength of nanocrystalline Cu films with thickness below 500 nm falls into the region between ~600 and ~900 MPa. Therefore, we think that the stresses between 420 and 640 MPa of the present Cu films during annealing are rather high values. The high-tension internal stresses will induced the development of dislocations. According to the above discussion, the electric field will further accelerate the increase in the dislocation density. As a result, the driving force of grain growth will be enhanced by the increasing density of vacancies and dislocations. Moreover, for metal films with high surface volume, the surface effect plays an important role on their properties and microstructure. Generally, a charged surface layer with thickness of several nanometers is induced by the external electric fields, which can create an additional energy barrier preventing the vacancies and dislocations from approaching the surface of the Cu films and increasing the level of internally stored energy.[28] Thus, the enhanced driving force by the coupling factor $f(E)\cdot\mu^{T/100\,°C}$ accelerates grain growth during annealing. The grain growth will be faster by imposition of the electric field than that of annealing only. It is noted that systematic experiments at various electric and temperature fields need to be performed in future work to reveal the intrinsic physical mechanism of grain growth induced by the electric field. Especially, it is important to treat the charged vacancy on the same atomistic level to quantitatively explain the effect.

In conclusion, the coupling effect of the external electric field on grain growth of nanocrystalline Cu films was studied at different annealing temperatures. The results from transmission electron microscopy and x-ray diffraction indicate that grain growth of Cu films is accelerated by the external electric field at different temperatures. A coupling factor $f(E)\cdot\mu^{T/100\,°C}$ accelerating grain growth is determined by theoretical deduction. The driving force increases due to the enhanced vacancy and dislocation density by the electric field, which is responsible for the accelerating grain growth.

This work was supported by the State Key Program for Basic Research of China (Grant No. 2004CB619305-2010CB631004) and the Natural Science Foundation of China (Grant No. 50831004).

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