INVESTIGATION OF SURFACE DIFFUSION IN Cu-Sn THIN FILMS

R. Halimi

Solid State Physics laboratory, Institute of Physics
University of Constantine-Algeria

Abstract

The surface diffusion in Cu-Sn thin films was investigated in the temperature range of 90-180°C by transmission electron microscopy and X-ray microanalysis technics. The samples were prepared by thermal evaporation in vacuum (10^{-6} Torr) on glass substrates. Copper films were deposited at 350°C and then Sn films were deposited on copper at room temperature. The thickness of the samples ranged between 2500 and 4000 Å. The diffusion parameters, namely the diffusion coefficient and activation energy were determined. It was established that these parameters depend upon the thickness of Sn films. By changing the Sn film thickness from 700 to 1400 Å, the coefficient of surface diffusion changes by two orders of magnitude and the activation energy changes by 0.2 eV.

Introduction

The high interest to study the diffusion process in thin films is stimulated by the wide applications in microelectronics of multilayer structures (1,2). surface mass transport presents a great importance because layered structures are generally disposed on a common substrate with micron spacings from each other. From a practical point of view, detailed study of lateral diffusion process in multilayer structures can considerably reduce their dimensions and increase their reliability and life time (3-5).

In the other side, the study of surface diffusion gives valuable information about the structure, surface microrelief, surface energy and the interaction of adsorbed atoms with films surface (6-9).

Experimental

In this work the surface diffusion in Cu-Sn thin films was studied by X-ray microanalysis and transmission electron microscopy technics. The samples were prepared by thermal evaporation in vacuum (10^{-6} Torr). Copper films were deposited at 350°C on glass substrates. The Sn films were deposited at room temperature on previously evaporated Cu films by using a special mask prepared by photolithography in order to obtain a sharp edge of the Sn film (Fig. 1).

The thickness of Cu-Sn samples was taken in the range of 2500-4000 Å. The samples were annealed in vacuum (10^{-6} Torr) in the temperature range of 90-180°C.

The structure of the films was studied by transmission electron microscope (STEM-200) with an operating accelerating voltage of 150 KV.

The distribution of Sn on the surface of the Cu film was studied by X-ray microanalysis method (10) using a Microscan-5 (operating accelerating voltage = 25 KV and current through the sample = 3×10^{-9} A).

Results and Discussion

For large surface areas of Cu and Sn components in the direction of diffusion (x) (a condition which is satisfied in our experiment: samples dimensions: 2.10^{-2} m x 10^{-2} m, extension of diffusion zone = 5×10^{-5} m), the problem of migration of adsorbed atoms on the surface becomes analogous to the diffusion problem in infinitless body. The distribution of adatoms (n) along the x axis is given by the error's integral:

$$n = n_0 \int_{\frac{x}{2\sqrt{D_s t}}}^{\infty} \exp(-y^2).dy \quad (1)$$

were, D_s - coefficient of surface diffusion
t - time

The concentration gradient of adatoms can be determined by the following expression:

$$\frac{dn}{dx} = \frac{n_0}{\sqrt{\pi}} \exp\left(-\frac{x^2}{4 D_s t}\right) \quad (2)$$

The quantity of diffused Sn atoms (q) through the unit of length which is perpendicular to the diffusion flow, for a time t, can be expressed as:

$$\ln q = \ln\left(\frac{n_0 D_s t}{\sqrt{\pi}}\right) - \frac{x^2}{4 D_s t} \quad (3)$$

Since the variation of intensity ΔI is proportional to the change of concentration , then

$$q \propto \int_x^{\infty} \Delta I.\, dx , \quad (4)$$

(Intensity I refers to the characteristic radiation of Sn obtained experimentally), i.e. q is proportional to the area S under the distribution curve I = I(x).

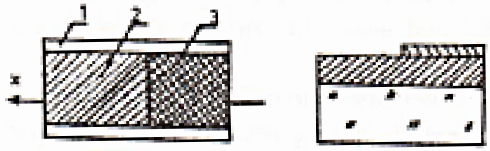

Fig.1. Form of investigated samples

1. Glass substrate
2. Copper film
3. Tin film

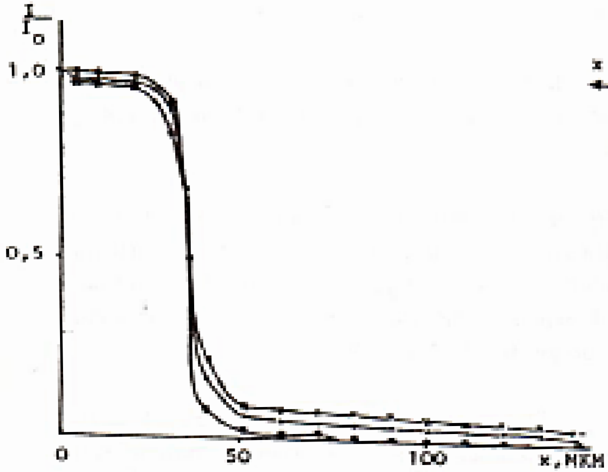

Fig.2. The Sn distribution on surface of Cu film

• — As prepared samples

+ — After 2 hours annealing at 150°C

x — After 4 hours annealing at 150°C

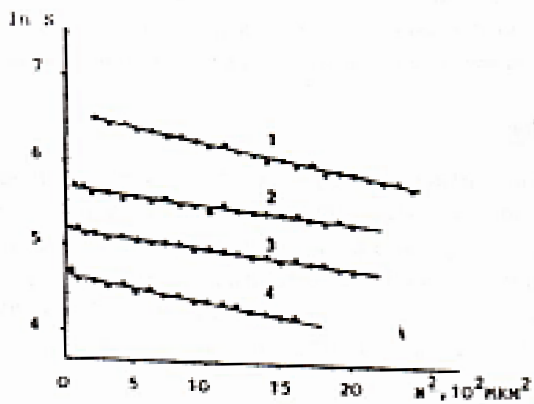

Fig.3. For the determination of diffusion coefficient in Cu-Sn thin films

1. T= 180°C, t= 1800 s , 2. T= 150°C, t= 7200 s
3. T= 120°C, t= 14640 s, 4. T= 90°C, t= 28.800 s

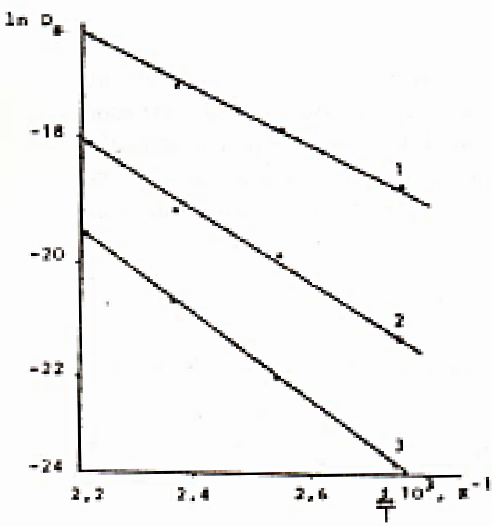

Fig.4. For the determination of activation energy

1- d_{Cu} = 2000 Å, d_{Sn} = 700 Å;

2- d_{Cu} = 2000 Å, d_{Sn} = 900 Å;

3- d_{Cu} = 2000 Å, d_{Sn} = 1400 Å.

Typical curves of Sn distribution are shown in Fig (2). It is clear that Sn is diffused along the surface of the Cu film.

From the curves ln S(x) where S∝ q, one can determine the coefficient of surface diffusion D_s according to equation (3) and Fig (3). The activation energy E_a was determined by the square method.

Obtained experimental results are given in Table 1. We can remark that for different temperatures and sample thicknesses the parameters of surface diffusion satisfy Arrhenius relation Fig. (4). In addition, by changing the Sn film thickness from 700 to 1400 Å, the coefficient of surface diffusion changes by two orders of magnitude and the activation energy changes by 0.2 eV (table 1).

The large dependance of E_a upon the film thickness is associated with the dependance of the grain size upon the thickness. This is verified experimentally by TEM studies which gave an average value of the grain size (Lg) increasing with the thickness (Lg increased from 5×10^{-8} m to 2×10^{-7} m for Sn films ranging from 700 to 1400 Å thick).

A comparison between the values of surface, grain boundary and bulk diffusion parameters is given in Table 2. It is clear from the table that D_s and D_{gb} are much higher tan D_v. This can be explained by the fact that atoms located on the surface and on the grain boundaries have less number of neighbour atoms than those atoms existing inside bulk of the material. Therefore, less energy is required to activate surface atoms than energy required for bulk atoms.

Conclusion

The surface diffusion in thin films of binary system Cu-Sn was studied by transmission electron microscope and X-ray microanalysis method. The diffusion parameters (D_s and E_a) were determined. It was established that the surface diffusion coefficient (D_s) and the activation energy (E_a) depend upon the thickness of Sn films. By changing the Sn film thickness from 700 to 1400 Å, D_s changes by two orders of magnitude and E_a changes by 0.2 eV.

References

1. **J.M. Poate, K.N. Tu and J.W. Mayer.** Thin films.Interdiffusion and Reactions, Wiley-Interscience, New York; 1978.

2. **V.M. Koleshko, V.F. Belitsky.** Mass transport in thin films, Sci. and Techn., Minsk (URSS), 1980.

3. **C. Weaver.** in Physics of thin films, vol. 6, Acad. Press, New York, 1971.

4. **E.M. Chpilevski**- Diffusion in thin films. DEP. BINITI, 1974, Nº 1923-74 DEP.

5. **A. Gangulee, P.S. HO, K.N. Tu.** Low temperature Diffusion and Applications to thin Films. Elsevier, Lausanne, 1975.

6. **L.C. Palatnik, V.K. Sorokin.** Material, science in microelectronics, Moscow, Energy, 1977.

7. **Ya. E. Guegouzin.** Surface Diffusion and Spreading, Moscow, Science, 1969.

8. **J.M. Blakely.** Surface Diffusion. M., Metallurgy, 1965.

9. **D.M. Skorow, A.I. Dachkovsky, V.N. Maskalets, V.K. Khijni, M. Atomedit.,** 1973.

10. **E.M. Chpilevski, R. Halimi, D.A. Gorbatchevski, I.M. Starchenko. Izvestia** Acad. Sci. RSSR. vol. 2. p. 114, 1984.

11. **V.A. Gorbatchev, S.M. Klotsman, Ya. A. Rabovsky, V.K. Talinsky, and A.N. Timofeev, Soviet Fiz.** Metal and Metalloved., V. 35, № 4, p. 889, 1973.

12. **P.L. Foguelson, Ya. A. Ougae, and I.A. Akimova.** Soviet Fiz. Metal and Metalloved, V. 37, № 5, p. 1107, 1974.

Table 1: Surface Diffusion Parameters in Cu-Sn Thin Films

Sample	T (ºC)	D_s (cm^2/s)	E_a (eV)
d_{cu} = 2000 A d_{sn} = 700 A	180 150 120 90	$4{,}5.10^{-9}$ $1{,}86.10^{-9}$ $8{,}38.10^{-10}$ $3{,}21.10^{-10}$	0,41 ± 0,05
d_{cu} = 2000 A d_{sn} = 900 A	180 150 120 90	$6{,}52.10^{-10}$ $1{,}96.10^{-10}$ $9{,}28.10^{-11}$ $2{,}18.10^{-11}$	0,52 ± 0,05
d_{cu} = 2000 A d_{sn} = 1400 A	180 150 120 90	$1{,}25.10^{-10}$ $3{,}77.10^{-11}$ $1{,}03.10^{-11}$ $2{,}29.10^{-12}$	0,63 ± 0,05

Table 2

Sample	D (cm^2/s)	E_a (eV)	T (ºC)	Reference
Cu-Sn thin films	$D_s \simeq 2.10^{-10}$	0,63	180	Present work
Cu-Sn thin films	$D_{gb} \simeq 2.10^{-13}$	0,96	180	/10/
Cu-Sn Monocrystal	$D_v \simeq 2.10^{-22}$	2	180	/11,12/

D_s - Surface diffusion coefficient

D_{gb} - Grain-boundary diffusion coefficient

D_v - Bulk diffusion coefficient

E_a - Activation energy

d - Film thickness