

# Investigation of interdiffusion in copper/nickel bilayer thin films

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## Abstract

Auger depth profiling technique, X-ray diffraction analysis, and scanning electron microscopy have been employed to study the interdiffusion in vacuum deposited copper/nickel bilayer thin films. An adaptation of the Whipple model was used to determine the diffusion coefficients of both nickel in copper and copper in nickel. The calculated diffusion coefficient is  $(2.0 \times 10^{-7} \text{ cm}^2/\text{s}) \exp(1.0 \text{ eV}/kT)$  for nickel in copper, and  $(6 \times 10^{-8} \text{ cm}^2/\text{s}) \exp(-0.98 \text{ eV}/kT)$  for copper in nickel. The difference between the diffusion parameters obtained in the present work and those extracted by other investigators is attributed essentially to the difference in the films microstructure and to the annealing ambient. It is concluded that interdiffusion in the investigated films is described by type B kinetics in which rapid grain-boundary diffusion is coupled to defect-enhanced diffusion into the grain interior. The present data raise a question about the effectiveness of nickel as a diffusion barrier between copper and the silicon substrate.

## 1 Introduction

The importance of understanding diffusion processes in thin films for controlling the quality of microelectronic devices, in terms of both efficiency and stability, does not need to be emphasized. Copper is widely used in microelectronics and silicon solar cells, but copper is known to be a fast diffuser into silicon substrate and this could deteriorate the p-n junction [1]. Also, the poor adhesion of copper with some kinds of substrates in chip-packaging devices could be a problem. Therefore, an intermediate metal such as nickel is deposited first to reduce the diffusion and to improve the adhesion between copper and its substrate.

Since the fabrication of integrated circuits involves thermal annealing of thin film systems at temperatures ranging from 473 K to 773 K, these systems can undergo diffusion processes, which result in a degradation of their performance. Diffusion in thin films can cause serious problems in microelectronic packing such as loss of bond strength, loss of solderability and loss of conductivity [2]. Therefore, the investigation of diffusion in thin film systems is of great importance. Diffusion in thin film is much faster than equilibrium diffusion in bulk materials since these films are characterized by a high density of defects such as dislocations, vacancies, and grain boundaries which act as paths of easy diffusion. So diffusion in thin films cannot be described by the extrapolation of data obtained for bulk materials at higher temperatures.

In thin films the change in concentration profiles due to interdiffusion can be studied by Auger electron depth profiling. The interdiffused samples are sputtered by argon ions and simultaneously the composition of the surface is measured by Auger electron spectroscopy [3]. The degree of interdiffusion in copper/nickel thin films is

of considerable interest in the microelectronics industry, so it has been extensively investigated [4-8], and it is still a subject of current researches [9-12] using a variety of analytical models and techniques. The objective of the present work is to study the interdiffusion in copper/nickel bilayer thin films emulating the fabrication processing conditions of typical chip-packaging module, using a modified Whipple model and employing Auger depth profiling (ADP) technique, X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM).

## 2 Experimental details

Nickel-copper bilayer thin films were deposited on highly cleaned [13] silicon (111) wafers by sequential evaporation, in single pump-down cycle, of pure (99.99%) nickel and pure (99.99%) copper in a vacuum of  $2 \times 10^{-6}$  mbar. Sequential evaporation in a single pump-down cycle is necessary to minimize interfacial oxides formation, which severely inhibit interdiffusion. The thickness of nickel layer was 150 nm and the thickness of copper layer was 300 nm. The deposition rate was 15 nm/min for nickel layer and 30 nm/min for copper layer. Since for thin films couples the grain structure is an important factor in controlling the rate of mass transport, the matrix metals were evaporated onto heated silicon (111) wafers at 383 K in order to stabilize the grain structure during diffusion. The substrate temperature was not raised above 383 K to prevent premature interdiffusion during deposition. After preparation, diffusion annealing was performed in a vacuum furnace of  $4 \times 10^{-6}$  mbar pressure at constant temperatures (473, 573, 673, and 773 K) for an annealing time between 5 min and 190 min.

Composition-depth profiles were obtained by Auger electron spectroscopy in combination with in situ argon ion sputtering. The Auger system used was a SAM 660 scanning Auger electron microprobe manufactured by Perkin Elmer and was operated at the following conditions and specifications. The basic vacuum in the analysis chamber was  $3 \times 10^{-10}$  mbar and during sputtering it was  $2 \times 10^{-8}$  mbar. The analysis area for the Auger signal was  $(100 \times 100) \mu\text{m}^2$ . The electron energy was 5 keV with a spot size of  $1 \mu\text{m}$  in a diameter and a current ranging between 500 and 600 nA. The samples were sputtered with 3 keV argon ions. The ion current was 800 nA with a spot size of  $800 \mu\text{m}$  in a diameter. The ions beam was scanned during sputtering in an area of  $(3 \times 3) \text{mm}^2$ .

X-ray diffraction analysis was carried out employing a Philips PW 1710 automated diffractometer using monochromated Cu  $K_{\alpha}$  radiation of  $1.5406 \text{ \AA}$  in wavelength. The X-ray tube was operated at a voltage of 40 kV and a current of 30 mA. Surface morphology and microstructure of the investigated films were tested using a JEOL scanning electron microscope model JSM-6400. The probe current was in the range  $10^{-10}$ - $10^{-7}$  A. The accelerating voltage of electron gun was 20 kV.

## 3 Results and discussion

An adaptation of the Hall *et al.* [14] model, which is based on Whipple's Fourier-Laplace transformation, was used to determine the diffusion coefficients of nickel in copper and copper in nickel. In this model, the average diffusion concentration ( $\bar{C}$ ) in the plane during the initial stage of diffusion can be expressed as

$$\frac{\bar{C}}{C_0} = \frac{8(Dt)^{1/2}}{L\pi^{1/2}} + \operatorname{erfc} \left[ \frac{y}{2(Dt)^{1/2}} \right] \left[ 1 - \frac{8(Dt)^{1/2}}{2\pi^{1/2}} \right] \quad (1)$$

where  $C_0$  is the time independent concentration at the interface,  $D$  denotes the diffusion coefficient,  $t$  is the diffusion time,  $L$  represents the grain size, and  $y$  is the distance normal to the original interface. The first term of Eq. (1) represents the plateau concentration, which is independent of  $y$  and proportional to  $t^{1/2}$ . The second term is appreciable only near  $y=0$  (original interface) and refers to the broadening of the concentration at the interface.

Auger electron spectroscopy in combination with in situ argon ion sputtering is the technique used in the present work to obtain the concentration profiles. Typical Auger depth profiles are shown in Fig.1. An obvious feature of Auger depth profiling curves is the nearly constant concentration at the most portions of the copper/nickel films except the interfacial portion. One can infer from this observation that diffusion through grain boundaries is extremely fast in comparison with diffusion through grain interiors. Rapid grain boundary diffusion means that the boundaries are constantly full of the diffusant, and the slower lattice diffusion causes a concentration gradient just near the interface. In general, it was noted that annealing causes a broadening of the concentration gradient at the interface, whereas a region of relatively constant concentration (plateau) throughout the remainder of the film was observed. This leads to the ability of extracting the diffusion coefficients by two methods. The first method is based on the plateau portion of the ADP spectrum, where the first term of Eq. (1) is dominant. Hence, the diffusion coefficient ( $D$ ) can be evaluated from the expression

$$D = \frac{\pi L^2}{64 t^2} \left( \frac{\bar{C}}{C_0} \right)^2 \quad (2)$$

The second method of calculating the diffusion coefficients depends on the interfacial concentration gradient of the ADP curve, in which the following equation [14].

$$D = \frac{1}{4\pi t} \left[ \left( \frac{100\%}{S_t} \right)^2 - \left( \frac{100\%}{S_0} \right)^2 \right] \quad (3)$$

can be used to evaluate the  $D$  value. In Eq. (3),  $S_t$  denotes the concentration gradient at the interface of sample annealed for time  $t$ , and  $S_0$  is the concentration gradient at the interface of non-heat-treated sample.  $S_0$  arises from the experimental limitations on the depth resolution, non-flatness of the interface, and interdiffusion during deposition (substrate temperature was 383 K).

The mean grain size ( $L$ ) of copper film was determined from the XRD linewidth of Cu (111) shown in Fig.2, and using the Langford and Wilson [15] modification for the Warren-Scherrer method. The calculated mean grain size was 145 nm. The polycrystalline nature of copper film and the grain size value were confirmed by SEM micrograph displayed in Fig.3. Substituting the appropriate values obtained from ADP, XRD and SEM analysis in Eq. (2) and Eq. (3) yields the diffusion coefficients of nickel in copper listed in Table 1.

Extrapolating of bulk data at higher temperatures [16] yields lattice diffusion coefficients of nickel in copper to be  $1.0 \times 10^{-19}$  cm<sup>2</sup>/s at 673 K and  $3.2 \times 10^{-16}$  cm<sup>2</sup>/s at 773 K. These values are order of magnitudes smaller than the diffusion coefficients of the investigated thin films. This clearly indicates that interdiffusion in polycrystalline thin films is enhanced by other mechanisms such as grain-boundary diffusion and defect diffusion. Grain-boundary diffusion alone is not sufficient to account for the

**Table 1** Diffusion coefficients of nickel in copper

Temperature (K)	D (cm <sup>2</sup> /s)
473	1.9×10 <sup>-18</sup>
573	4.3×10 <sup>-16</sup>
673	5.2×10 <sup>-15</sup>
773	2.8×10 <sup>-14</sup>

detected concentrations of the diffusant nickel or copper observed in Fig. 1, because grain boundaries constitute only 1% of the total area [14]; even in the boundaries one could not expect more than 50 at. % solute, and hence grain boundary diffusion can account only for ~0.5 at. % which is a small portion of the 5-15 at. % concentrations measured in Fig.1. Therefore, an additional diffusion enhancement mechanism should be involved such as diffusion through a high density of vacancies and dislocations. The polycrystalline and highly defective nature of the investigated films is depicted in Fig. 4.

The diffusion coefficients of nickel in copper were plotted according to the Arrhenius equation:

$$D = D_0 \exp(-Q / kT) \quad (4)$$

as shown in Fig. 5. The activation energy (Q) and the pre-exponential factor (D<sub>0</sub>) were evaluated from the least-squares fitting as listed in Table 2 in comparison with the corresponding results of other researchers. The very low Q value of 1.0 eV extracted from the present work in comparison with Q value of 2.32 eV obtained by Almazouzi *et al.* [7] for nickel in single crystalline copper, gives further evidence that grain boundaries and high defects density play a dominant role in the diffusion process of the investigated thin films. The large difference between the diffusion parameters extracted by various workers can be attributed essentially to the difference in the microstructure of the investigated films which is controlled by the preparation conditions [12], and to the heat-treatment ambient.

**Table 2** The activation energy (Q) and pre-exponential factor (D<sub>0</sub>) of nickel in copper obtained in the present work in comparison with the results of other workers.

Q (eV)	D (cm <sup>2</sup> /s)	Investigator
1.00	2.0×10 <sup>-7</sup>	Present work
1.38	2.6×10 <sup>-6</sup>	Johnson <i>et al.</i> [4]
1.10	1.4×10 <sup>-10</sup>	Venos <i>et al.</i> [5]
2.32	6.2×10 <sup>-1</sup>	Almazouzi <i>et al.</i> [7]

Using the same analysis described above, the average diffusion coefficients of copper in nickel extracted from the interfacial gradient method and the plateau method were determined as listed in Table 3. These D values were plotted against 1/T as in Fig. 6, and the resulting Q and D<sub>0</sub> values from the least squares fitting are shown

in Table 4 in comparison with the corresponding value reported by Johnson *et al.* [4]. The obvious difference in Q value shown in Table 4 gives another evidence that the diffusion kinetics are strongly affected by the microstructure of the investigated films, as it was also emphasized by Wehr and Rylski [17].

**Table 3** Diffusion coefficient of copper in nickel

Temperature (K)	D (cm <sup>2</sup> /s)
473	1.7×10 <sup>-18</sup>
573	2.2×10 <sup>-16</sup>
673	2.5×10 <sup>-15</sup>
773	2.1×10 <sup>-14</sup>

The present work shows that nickel satisfies considerable requirement of the diffusion barrier reported by Nicolt and Bartur [18]. However, a relatively large concentration of copper which penetrates the nickel layer to the silicon substrate, as shown in Fig. 1, raises a question about the effectiveness of nickel as a diffusion barrier between copper and the silicon substrates.

**Table 4** The activation energy (Q) and pre-exponential (D<sub>0</sub>) values for copper in nickel obtained in the present work compared with those extracted by Johnson *et al.* [4].

Q (eV)	D (cm <sup>2</sup> /s)	Investigator
0.98	6×10 <sup>-8</sup>	Present work
1.51	5.2×10 <sup>-8</sup>	Johnson <i>et al.</i> [4]

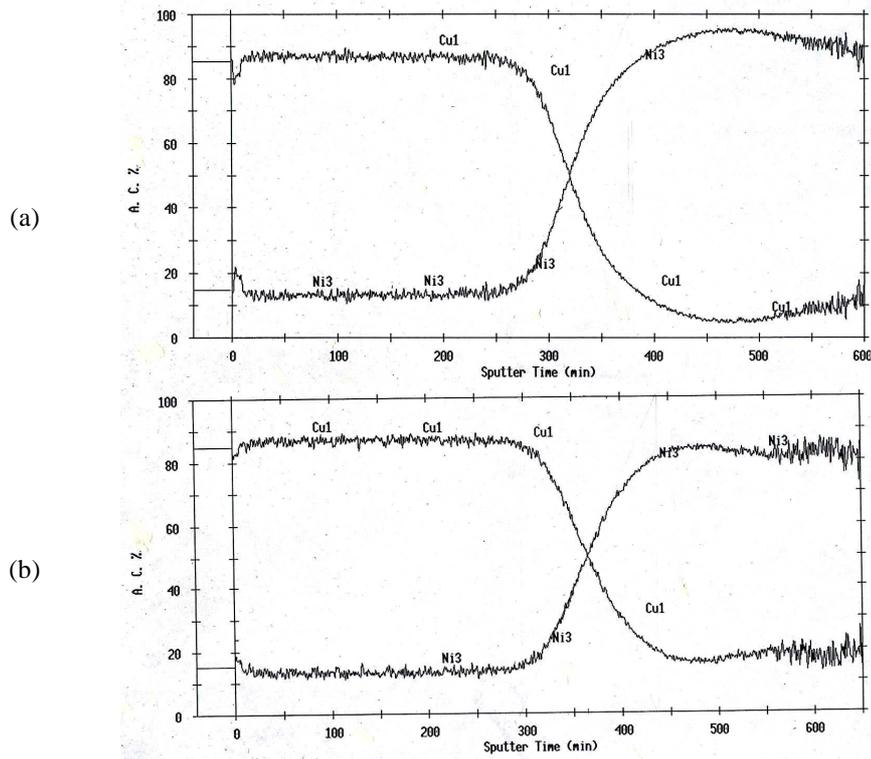
### 3 Conclusions

The diffusion parameters of thin film systems are strongly affected by the film microstructure and by the heat-treatment ambient, and this may give an interpretation for the larger difference in the diffusion parameters extracted by various investigators for the same thin film system. Grain boundaries and other kinds of crystal defects play a dominant role in the diffusion process. Interdiffusion in the investigated copper/nickel thin films can be described by type B Kinetics [19] in which rapid grain-boundary diffusion is coupled to defect-enhanced diffusion into the grain interior. In spite that nickel satisfied considerable equipments of the diffusion barrier, the concentration profiles reveals that nickel cannot be regarded as an ideal diffusion barrier between copper and the silicon substrate.

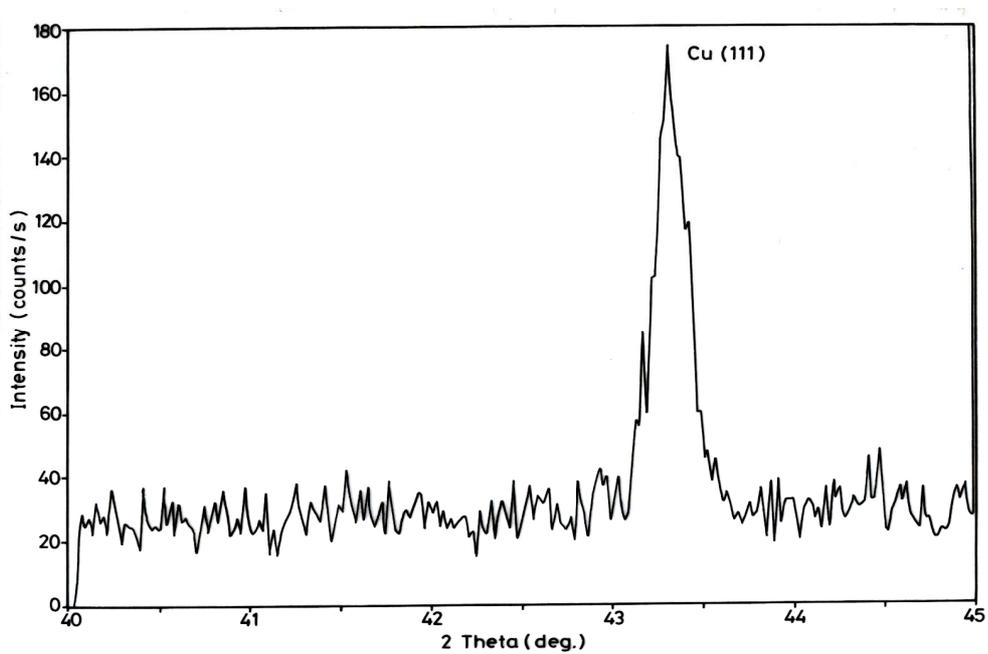
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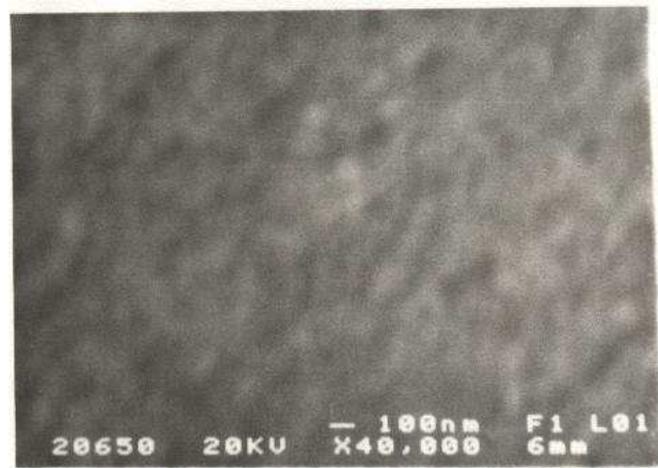
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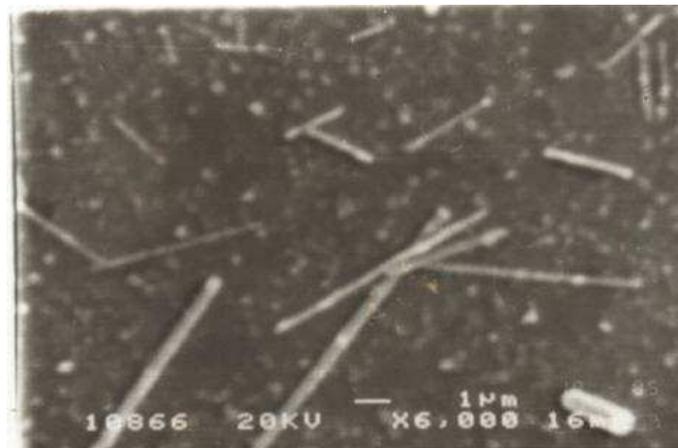
**Fig.1** Atomic concentrations of copper and nickel against sputter time for (a) sample annealed at 573 K for 25 min, and (b) sample annealed at 673 K for 85 min.



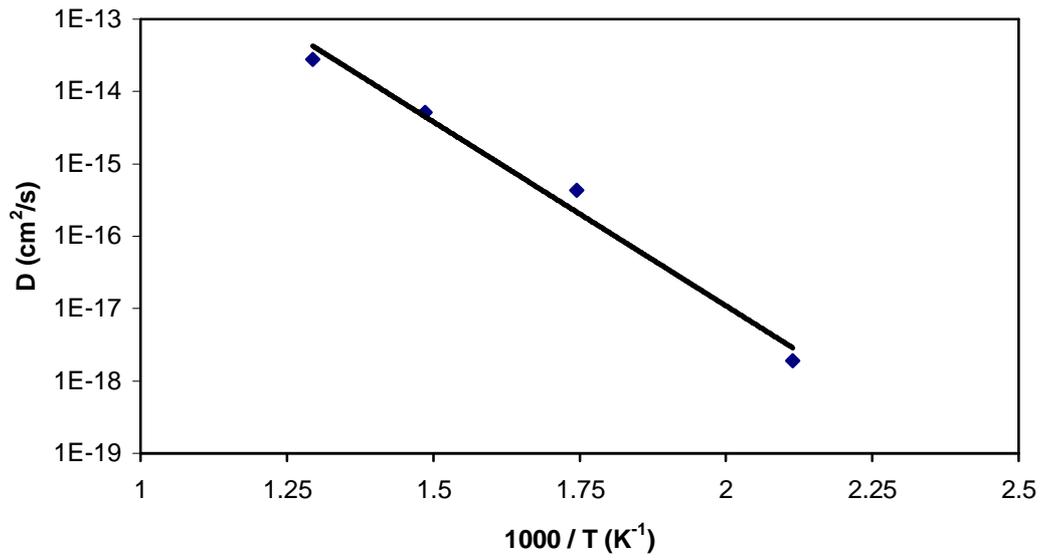
**Fig.2** X-ray diffraction spectrum of as deposited copper/nickel thin films.



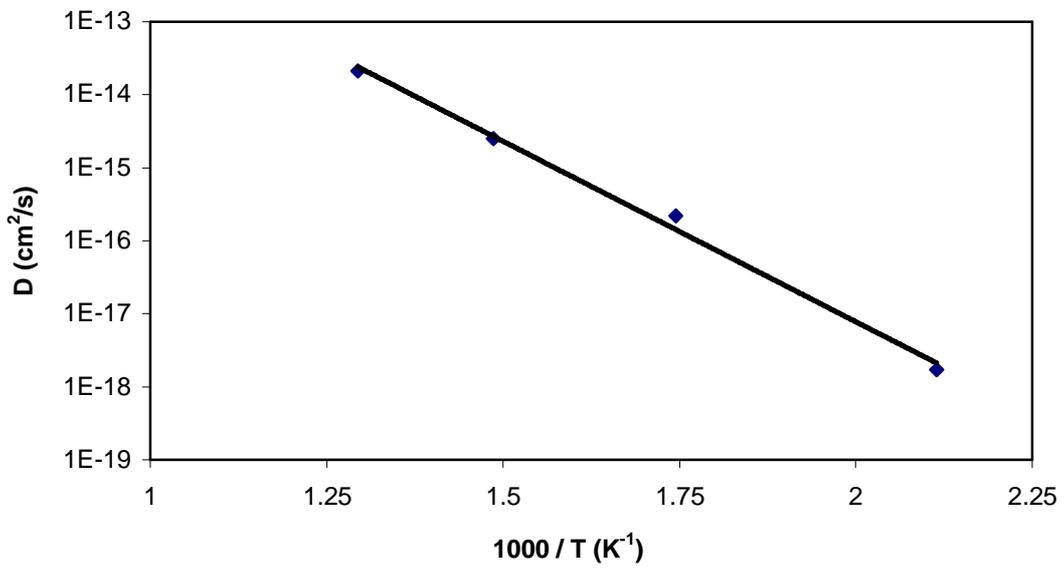
**Fig.3** Scanning electron micrograph of as deposited copper/nickel thin films.



**Fig.4** Highly defective and polycrystalline nature of the investigated copper/nickel thin films.



**Fig.5** Arrhenius plot for the diffusion coefficients of nickel in copper.



**Fig.6** Arrhenius plot for the diffusion coefficients of copper in nickel.