

Interdiffusion coefficients and conductivity in gold/nickel bilayer thin films on silicon(111) wafers[†]

A. M. Abdul-Lettif,* N. N. Rammo and M. N. Makadsi

College of Science, Baghdad University, Baghdad, Iraq

Received 23 October 2000; Revised 5 December 2000; Accepted 8 January 2001

Interdiffusion in the gold/nickel bilayer thin films deposited on silicon(111) wafers in the temperature range 200–500 °C has been studied using x-ray photoelectron spectroscopy (XPS), sheet resistance measurements (SRM) and x-ray diffraction. Two independent methods have been used to determine the diffusion coefficients: the accumulation concentration of nickel on the gold surface using XPS; and the variation of sheet resistance as a function of annealing time and temperature.

The diffusion coefficients deduced from XPS and SRM are $(4.0 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}) \exp(-0.79 \text{ eV/kT})$ and $(4.8 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}) \exp(-0.83 \text{ eV/kT})$, respectively. It is shown that diffusion of nickel through the gold layer causes a considerable loss in conductivity of the bilayer thin films. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: interdiffusion; gold; nickel; thin films

INTRODUCTION

Gold is often used as a conductor and bonding pad material in electronic microcircuits because of its low resistivity, good corrosion resistance and good bondability. However, gold does not adhere well to the silicon or its oxides commonly used for microcircuits.¹ Therefore, a thin layer of reactive material, such as chromium or nickel, is placed on the substrate prior to the deposition of gold to assure good adhesion.

During fabrication, metallized devices are often processed at temperatures of 200–500 °C,² where diffusion may occur^{3–6} and degrade the performance of the device. Evaluation of the extent of interdiffusion is frequently monitored using resistivity measurements,^{7–12} because changes in resistivity are of particular concern for device applications. In the present work interdiffusion in Au/Ni bilayer thin films deposited on Si(111) wafers is investigated using two independent methods: the accumulation concentration of nickel on the gold surface by XPS; the variation of sheet resistance as a function of annealing time and temperature.

EXPERIMENTAL

Starting materials were high-purity gold (99.99%) and nickel (99.99%). Two sets of samples of Au/Ni bilayer thin films were prepared by thermal evaporation under an uninterrupted vacuum of 2×10^{-6} mbar: an inner Ni layer of 200 nm thickness deposited at a rate of 25 nm min^{-1} and

an outer Au layer of 100 nm thickness deposited at a rate of 24 nm min^{-1} with a substrate temperature of 100 °C. The first set of samples were deposited on smooth and highly cleaned¹³ Si(111) wafers of $10 \times 10 \text{ mm}$ dimensions to be examined by XPS. The second set of samples were deposited on thermally oxidized Si(111) wafers with an insulating SiO₂ layer to permit resistivity measurements by the four-point probe technique.

The Au/Ni couples were annealed at 200, 300, 400 and 500 °C for times of 1–7 h in a vacuum furnace (10^{-6} mbar) to reduce the oxidation of Ni that diffuses into the Au layer.

Selected samples were examined by a Riber-LAS-4000 x-ray photoelectron spectrometer under the following conditions: Mg anode as an x-ray source at an operation power of 340 W; the electron energy analyser was a MAC-2 with an energy step of 0.5 eV and an energy resolution of 0.8 eV; the pressure in the analysis chamber was 3×10^{-9} mbar; and depth profiling was accomplished by sputtering with Ar⁺ ions of 4.5 keV energy.

Sheet resistance of as-deposited and annealed samples was measured by an automated Veco FPP 500 four-point probe apparatus.

X-ray diffraction analysis was achieved by a Philips PW 1710 automated diffractometer using monochromated Cu K_α radiation of 1.5406 Å in wavelength.

RESULTS

Diffusion parameters of Ni through Au calculated via the two methods are given below.

Surface accumulation method

Depending on Wipple's Fourier-Laplace transformations, Johnson *et al.*¹² have used the following expression that

*Correspondence to: A. M. Abdul-Lettif, College of Science, Babylon University, Hilla, Iraq.

[†]Paper presented at APSIAC 2000: Asia-Pacific surface and Interface Analysis Conference, 23–26 October 2000, Beijing, China.

relates the diffusant concentration (\bar{C}) with the diffusion coefficient (D) as

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

where C_0 denotes the time-independent concentration at the interface, y denotes the direction normal to the original interface, L is the grain size and t is the diffusion time. The first term in Eqn. (1) denotes the plateau concentration, which is independent of y . The second term is noticeable only near the interface ($y = 0$).

The concentrations were obtained from quantification of the area under the peaks of Ni and Au in the XPS spectra (Fig. 1) using the relative sensitivity factor for each peak.¹⁴ The concentration measurements at three different depths (at the surface, at nearly 24 nm and at nearly 48 nm from the surface) for each sample showed no obvious variation in the diffusant material concentration, which permits the determination of D values from the first term of Eqn. (1).

The mean grain size was determined from the x-ray linewidth of Au(111) measured by x-ray diffraction (as in Fig. 2) using the Warren-Scherrer method¹⁵ and taking into account the modification to this method published by Langford and Wilson.¹⁶ The calculated mean grain size was ~ 58 nm.

The diffusion coefficients extracted from XPS analysis are plotted according to the Arrhenius equation ($D = D_0 \exp(-Q/kT)$) as shown in Fig. 3, and the activation energy

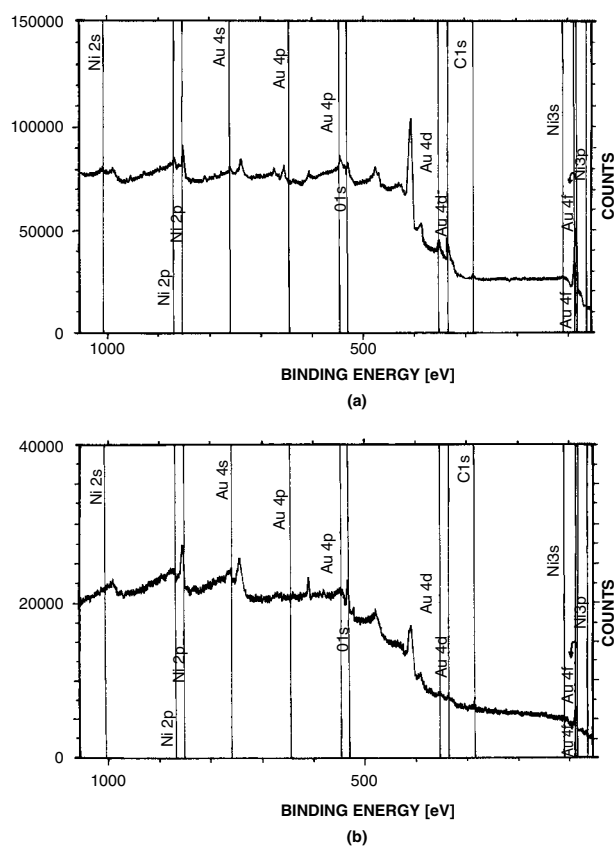


Figure 1. The XPS survey spectra of two Au/Ni thin films: (a) annealed at 300 °C for 4 h; (b) annealed at 500 °C for 1 h.

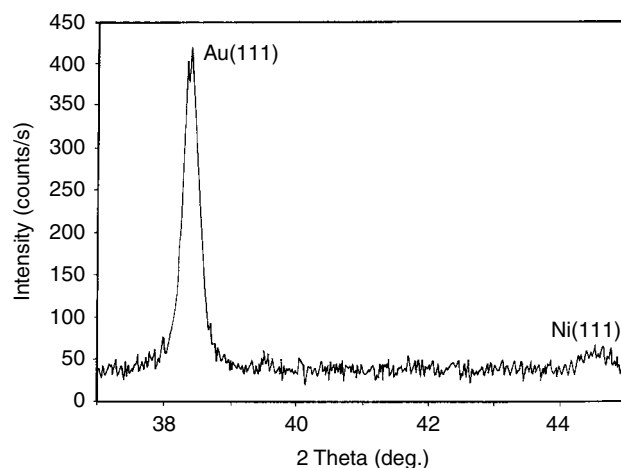


Figure 2. X-ray diffraction spectrum of as-deposited Au/Ni thin films.

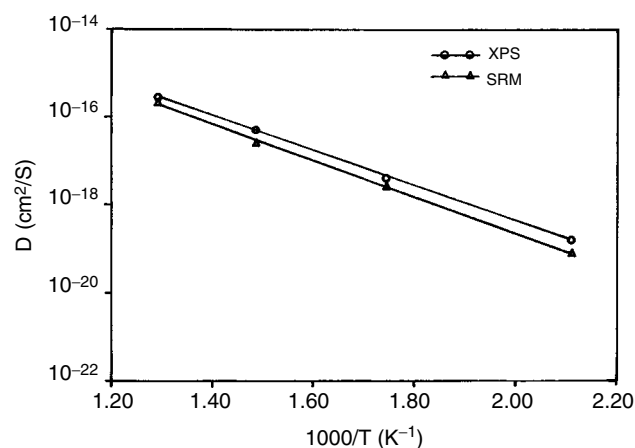


Figure 3. Arrhenius plots of diffusion coefficients of Au/Ni thin films deduced from XPS and sheet resistance measurements (SRM).

(Q) and the pre-exponential factor (D_0) are determined from least-squares fitting as listed in Table 1.

Resistance variation method

It is well known that the resistivity of a metal varies with the impurity concentration; this, in turn, is diffusion dependent in a bilayer system. Hall *et al.*⁷ have derived an expression relating the relative change in resistance ($\Delta R/R_0$) to the diffusion coefficient (D) as follows

$$\frac{\Delta R}{R_0} = \frac{4aC_0}{\pi^{1/2}L} (Dt)^{1/2} \quad (2)$$

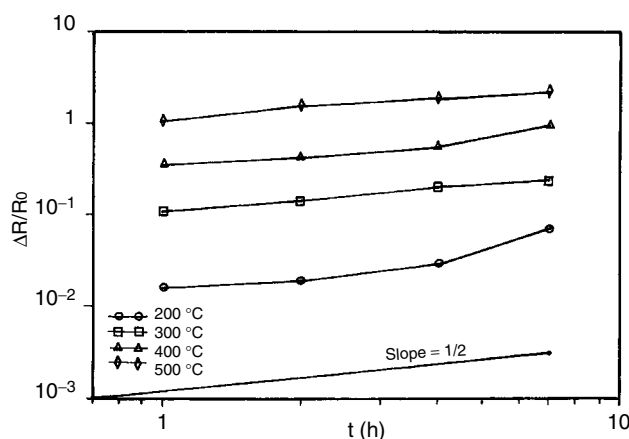
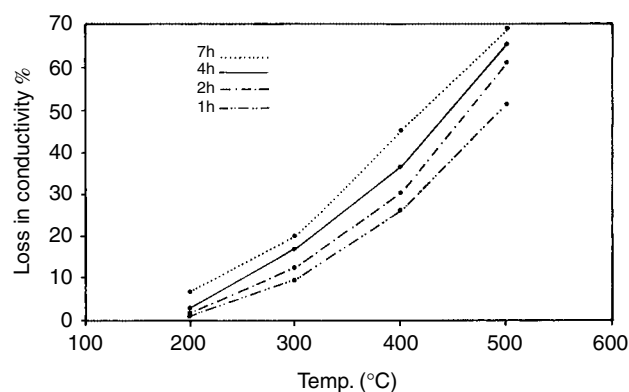
where a is a proportionality constant, C_0 is the saturation value of concentration and L and t are the mean grain size and diffusion time, respectively.

The relative changes of sheet resistance as a function of time for Au/Ni thin films annealed at 200, 300, 400 and 500 °C are plotted in Fig. 4. From Fig. 4 the saturation value of $\Delta R/R_0$ could be estimated to be ~ 3 and this value is substituted for aC_0 in Eqn. (2) as in Ref. 7.

The average diffusion coefficients are Arrhenius plotted, as in Fig. 3, and the least-squares fitting yielded the Q and D_0 values listed in Table 1.

Table 1. Comparison of diffusion parameters of Au/Ni thin films from XPS and sheet resistance measurements

Method	Q (eV)	D_0 ($\text{cm}^2 \text{s}^{-1}$)	Remarks	Investigator
Surface accumulation	0.79	4.0×10^{-11}	Au(100 nm)/Ni(200 nm) annealed in vacuum	Present work
Resistance variation	0.83	4.8×10^{-11}	Au(100 nm)/Ni(200 nm) annealed in vacuum	Present work
Surface accumulation	1.17	3.0×10^{-3}	Au(300 nm)/Ni(40 nm) annealed in air	Swartz <i>et al.</i> ⁶

**Figure 4.** Relative change of sheet resistance as a function of time for Au/Ni thin films annealed at 200, 300, 400 and 500 °C.**Figure 5.** Percentage loss in conductivity of Au/Ni thin films as a function of temperature for samples annealed for 1, 2, 4 and 7 h.

Calculations of the percentage loss in conductivity of the bilayer films as a function of annealing time and temperature as shown in Fig. 5, clearly indicating that Ni diffuses readily through the Au layer.

DISCUSSION

Because no concentration gradients at depths of ~ 48 nm from the Au surface for each annealed sample were observed, the satisfactory assumption arises that diffusion through grain boundaries is extremely fast compared with diffusion through grain interiors. Rapid grain boundary diffusion means that the boundaries are constantly full of the diffusant

(Ni), whereas slower lattice diffusion causes a concentration gradient just near the interface.

Another important observation deduced from XPS analysis is the large Ni concentration level of >30 at.% for a sample annealed at 500 °C for 1 h and 20 at.% for a sample annealed at 400 °C for 2 h. These large atomic concentrations of the diffusant material cannot be attributed to the lattice diffusion mechanism alone, because the diffusion coefficient extrapolated from bulk data at higher temperatures is $5.9 \times 10^{-16} \text{ cm}^2 \text{s}^{-1}$ at 400 °C.¹⁷ The corresponding diffusion length $(Dt)^{1/2}$ of only 41 nm clearly indicates that this mechanism is not enough to account for the measured Ni concentrations or even the extent of interdiffusion observed. The grain boundary diffusion also is not sufficient to account for the measured concentrations of Ni. Geometrically, grain boundaries comprise a fraction of the total area given by w/a ,⁷ where w denotes the effective boundary width, which was estimated to be ~ 1 nm,¹⁸ and a is the mean grain radius ($L/2$), which was calculated to be 29 nm. Thus the grain boundaries constitute only 3.4% of the total area of the Au surface. The maximum solute within a boundary can be assumed to be 50%; even in this case, the grain boundaries could contribute to only 1.7 at.% of Ni at the Au surface. Thus, it is evident that diffusion might be accelerated by other mechanisms such as diffusion along a high density of vacancies and dislocations, which is predicted to be present in thin films structures¹⁹ and could be inferred from the high R_s value of the as-deposited Au/Ni samples (0.189Ω) compared with the calculated value (0.135Ω) using bulk data.

It is obvious from Fig. 4 that the slope of $\Delta R/R_0$ vs. t curves is roughly 1/2. This suggests a diffusion-controlled mechanism, as Eqn. (2) indicates. However, there is a tendency to approach saturation for samples annealed at 500 °C for longer times. The departure of the aforementioned curves from linearity and the 1/2 value slope can be attributed mainly to the changes in grain size,²⁰ strain⁷ and density of defects²¹ that had been caused by heat treatment.

Comparing the average Q value of 0.81 eV from the two methods with the corresponding value of 1.81 eV reported from bulk diffusion data¹⁷ gives further evidence that grain boundaries and high defect density play a dominant role in the diffusion process of the investigated films.

Table 1 shows that there is a disagreement between the diffusion parameters extracted from the present work and those reported by Swartz *et al.*⁶ The discrepancy can be attributed essentially to the difference in the microstructure of the investigated films,²² which is controlled by the

preparation conditions and the heat treatment environment. Swartz *et al.* annealed their samples in air and the driving force for diffusion in this case is the oxidation of Ni at the Au surface.

The present work shows that Ni satisfies the considerable requirements of the diffusion barrier reported by Nicolet and Bartur,²³ but the major disadvantage of Ni in this respect is that the diffusion of Ni through the Au layer causes a significant loss of conductivity of the bimetallic films system, as is obvious from Fig. 5, which may be due partly to the thickness of the Au film (100 nm) combined with the Ni film (200 nm).

CONCLUSIONS

From this study, it can be concluded that:

- (1) The sheet resistance method yields diffusion parameters that are in good agreement with those obtainable from XPS analysis and can be regarded as a reliable approach to diffusion studies.
- (2) Grain boundaries play a dominant role in the diffusion process of the investigated Au/Ni thin films.
- (3) Both lattice diffusion and grain boundary diffusion are not sufficient to account for the detected concentration of Ni at the Au surface. Thus, a defect-assisted diffusion mechanism is necessary to explain the detected amount of Ni. The low Q value in the Au/Ni thin films when compared with the corresponding value of the bulk material is also consistent with diffusion via a defect mechanism.
- (4) Diffusion of Ni through the Au layer causes significant loss in conductivity and raises the question of the effectiveness of Ni as an ideal diffusion barrier in thin Au films, as was concluded by Kurinec *et al.*²⁴

Acknowledgements

It is a pleasure to acknowledge the assistance of H. R. Al-Azzawi and L. K. Abood.

REFERENCES

1. Holloway PH, Nelson CC. *Thin Solid Films* 1976; **35**: L13.
2. Chao Y-K, Kurinec SK, Toor I, Shillingford H, Holloway PH. *J. Vac. Sci. Technol.* A5 1987; 337.
3. Tompkins HG, Pinnel MR. *J. Appl. Phys.* 1977; **48**: 3144.
4. Hall PM, Morabito JM. *Thin Solid Films* 1978; **53**: 175.
5. Brady TE, Hovland CT. *J. Vac. Sci. Technol.* 1981; **18**: 339.
6. Swartz WE, Linn JH, Ammons JM, Kovac MG. *Thin Solid Films* 1984; **114**: 349.
7. Hall PM, Morabito JM, Poate JM. *Thin Solid Films* 1976; **33**: 107.
8. Johnson BC, Bauer CL, Jordon AG. *J. Vac. Sci. Technol.* 1979; **16**: 128.
9. Suni I, Nicolet M-A, Maenpaa M. *Thin Solid Films* 1981; **79**: 69.
10. Sen SK, Kluge-Weiss PM, Bauer CL. *Thin Solid Films* 1981; **82**: 299.
11. Munitz A, Komen Y. *Thin Solid Films* 1984; **112**: 139.
12. Johnson BC, Bauer CL, Jordon AG. *J. Appl. Phys.* 1986; **59**: 1147.
13. Uppal PN, Kroemer H. *J. Appl. Phys.* 1985; **58**: 2195.
14. Riggs WM, Parker MJ. In *Methods of Surface Analysis*, Czanderna AW (ed.). Elsevier: Amsterdam, 1975; Ch. 4, 110.
15. Klug HP, Alexander LE. *X-ray Diffraction Procedure for Polycrystalline and Amorphous Materials* 2nd (edn). John Wiley: Chichester, 1974.
16. Langford JI, Wilson AJC. *J. Appl. Crystallogr* 1978; **11**: 102.
17. Murch GE, Breff CM. In *Diffusion in Solid Metals and Alloys*, Mehrer H (ed.). Springer-Verlag: Berlin, 1990; Ch. 5, 292.
18. Canon RF, Stark JP. *J. Appl. Phys.* 1969; **40**: 4361.
19. Balluffi RW, Blakely JM. *Thin Solid Films* 1975; **25**: 363.
20. Rijks ThGSM. *PhD Thesis*, Eindhoven University of Technology, 1996.
21. Berry RW, Hall PM, Harris MT. *Thin Film Technology* Van Nostrand: New York, 1968.
22. Abdul-Lettif AM. *PhD Thesis*, University of Baghdad, 1997.
23. Nicolet M-A, Bartur M. *J. Vac. Sci. Technol.* 1981; **19**: 786.
24. Kurinec SK, Toor I, Chao Y-K, Shillingford H, Holloway P, Ray S, Beckham K. *Thin Solid Films* 1988; **162**: 247.