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Investigating the Formation Mechanisms of $Cu_{0.83}Si_{0.17}$ Intermetallic Phase Formed at Cu-Si and Cu-(5at%)Nb/Si Interfaces

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ABSTRACT

A study of intermetallic compound formation at the interface between copper thin film and silicon substrate is presented in this work. Two systems; Cu/Si and Cu-(5at%) Nb/Si, were studied. From the intermetallics formed at the interfaces of two systems; as a model, formation mechanisms of $Cu_{0.83}Si_{0.17}$ with and without niobium impurity were examined. Variations in values of parabolic rate constants and activation energies with Nb impurity content were determined. The samples were annealed at different temperatures and time intervals after vacuum deposition of the films. X-Ray, Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) analysis showed the sequential formation of several intermetallic phases at the interfaces. Using this data, a model had been given about the formation of the observed intermetallic phases.

Key Words: *Intermetallics, thin metal films, impurity effect, reaction rate constants.*

1. INTRODUCTION

Thin films had found usage area in different subjects from electronis, textile to glass and dye industry and related works are being carried on. [1-4] Titanium dioxides's self-cleaning effect has been broadly used in textiles, paints, windows, residual water treatment, amongst various other photocatalytic applications. Polymer substrates have found their way in the semiconductor industry as a base layer for flexible electronics, as well as in sensor and actuator applications[5]. In lithium-ion batteries, nanocrystalline intermetallic alloys, nanosized composite materials, carbon nanotubes, and nanosized transition-metal oxides are all promising new anode materials, while nanosized $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$, and $LiMn_2O_4$ show higher capacity and better cycle life as cathode materials than their usual larger-particle equivalents [6]. The films; layer by layer deposition of zirconium oxide onto silicon, have been studied for their dielectric properties to understand the parameters leading to dense films with high dielectric constant [7]. Due to the increasing use of thin films in

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electronics, either as complete thin film circuits or more generally as interconnections & contacts in integrated circuits; diffusion in thin films has received significant attention [8-15]. Agillan and his friends determined that when thicknesses of $CuInSe_2$ thin films increases activation energies of the films decreases [16]. Quang PH and Yu SC investigated effect of substrate temperature to the activation energy of $Al_{0.87}Mn_{0.13}N$ thin film and concluded that activation energy of the film decreases with increased substrate temperature [17]. M.A. Aksu, M.E. Yakıncı and A. Güldeste showed that Co addition to MgB_2 thin film decreases in activation energy. [18] Fadel M, Sedeek K and Hegab NA concluded that Sn addition to $Ge_{1-x}Sn_xSe_3$ thin film decreases activation energy [19]. Cupper thin films are being investigated for the importance in microelectronic devices. Intermetallic compound formation at the interface between cupper thin film and silicon substrate is presented in this work. Two systems; Cu/Si and Cu-(5at%)Nb/Si, were studied.

2. EXPERIMENTAL OVERVIEW

Substrates preparation, vacuum coating of these substrates with evaporant, heat treatment of the films, examining the phases formed at the Cu/Si or Cu-(5at%)Nb/Si interface by using X-Ray Diffraction and investigating the surface morphology and microstructure of the film samples, SEM and EDS techniques were followed. The vacuum chamber loaded with evaporant (Cu or Cu-(5at%)Nb were used as evaporant) after silicon substrates cleaned with acetone. These films obtained by evaporating Cu or Cu-(5at%)Nb under vacuum around 10^{-5} torr with small fluctuations in a vacuum deposition unit (Nanotech Thin Films Ltd., Model Microprep 300-S, Manchester, UK) [20].

Cu-(5at%)Nb alloy casting was achieved under argon gas atmosphere at about 1800 ^{0}C by using a centrifugal casting machine, Manfredi Neutromag Digital. Cu and Nb were melted by induction heating by using ceramic based sintered special crucible having 2.564 cm^3 maximum capacity in the steel mold. During casting water cooled copper coils were used and temperature was measured by pyrometer. After coating; the films were annealed in a horizontal alumina tube furnace equipped with a programmable controller (ABB Kent Taylor-Commander 3000) under argon gas flow with annealing times ranging from 2 hours to 4 hours at temperatures between 400-600^{0}C. The heating and cooling rates were set to +10^{0}C/min and -1.5^{0}C/min, respectively.

3. RESULTS AND DISCUSSION

3.1. Cu/Si System

Cu films having 0.68μm thickness were deposited on silicon substrates and they were annealed at different temperatures; 400^{0}C, 500^{0}C and 600^{0}C for 2 h, 2.5 h, 3 h, 3.5 h and 4 h. Intermetallic phases; $Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η formed sequentially at the film-substrate interface. The forth layer; (Cu, Si)(Si at%21.2), formed when Cu film was annealed at 600^{0}C for 2.5 h, addition to those three layers which were annealed at 500^{0}C for 3.5 h. These layers were identified from X-Ray, SEM micrograph and EDS spectra. Phases formed at the interface are shown in Table 1.

Table 1. Phases formed during annealing of Cu films on Si substrates for different temperatures and times (constant thickness of 0.680 μm).

No	Heat Treatment	Phases Observed
1	As-deposited	Cu and Silica
2	400^{0}C, t=2 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η
3	400^{0}C, t=2.5 h	Cu, $Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η
4	400^{0}C, t=3 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η
5	400^{0}C, t=3.5 h	Cu, $Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, SiO_2
6	400^{0}C, t=4 h	Cu, $Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η
7	500^{0}C, t=2 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, SiO_2
8	500^{0}C, t=2.5 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, SiO_2
9	500^{0}C, t=3 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, SiO_2
10	500^{0}C, t=3.5 h	Cu,$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, (Cu,Si)(Si at%21.2)
11	500^{0}C, t=4 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, (Cu,Si)(Si at%21.2), SiO_2
12	600^{0}C, t=2 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, SiO_2
13	600^{0}C, t=2.5 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η, (Cu,Si)(Si at%21.2), SiO_2
14	600^{0}C, t=3 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, SiO_2
15	600^{0}C, t=3.5 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, SiO_2
16	600^{0}C, t=4 h	$Cu_{0.83}Si_{0.17}$

X-Ray diffractograms of Cu films grown on silicon substrate, as-deposited and annealed for 2 h, 2.5 h, 3 h, 3.5 h and 4 h at 500^0C, shown in Figure 1. From the intermetallics formed at the interface as an example, growth kinetics of $Cu_{0.83}Si_{0.17}$; which occured first as shown in Figure 2.a by number 1, was examined. EDS spectrum of the first layer and second layer are also shown in Figure 2.b and 2.c. SEM micrograph of 0.68µm thick Cu film grown on silicon substrate annealed for 3.5 h at 500^0C showing the 1st , 2nd and 3rd layers is given in Figure 3.a. EDS spectra of the same film showing the general elemental distribution belongs to these three layers are shown in Figure 3.b, 3.c and 3.d. The thickness measurements of $Cu_{0.83}Si_{0.17}$ phase were carried out by using SEM micrographs.

Cu/Si System

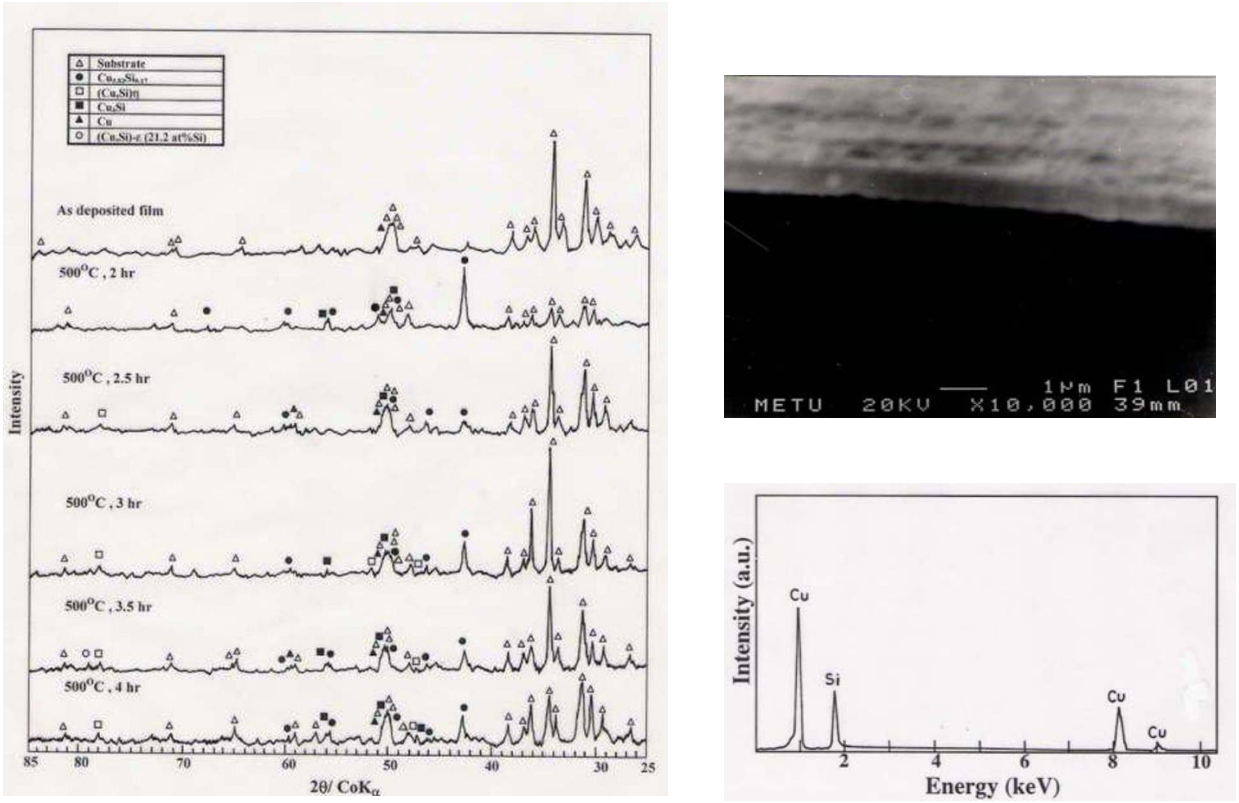

Figure 1 .a-) X-Ray diffractograms of Cu films grown on silicon substrate, as-deposited and annealed for 2 h, 2.5 h, 3 h, 3.5 h and 4 h at 500^0C; b-) SEM micrograph of 0.68 µm thick Cu film grown on silicon substrate as-deposited; c-) EDS spectrum of the same film.

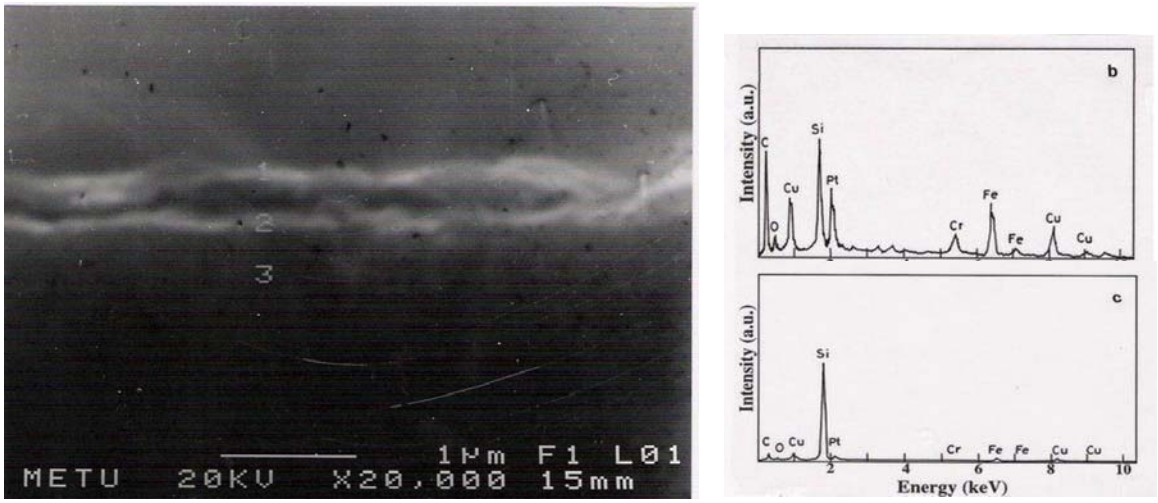

Figure 2.a-) SEM micrograph of 0.68 µm thick Cu film grown on silicon substrate annealed for 2.5 h at 500^0C showing the 1st, 2nd and 3rd layers. EDS spectrum of the same film showing the general elemental distribution which belongs to b-) 1st layer, c-) 2nd layer.

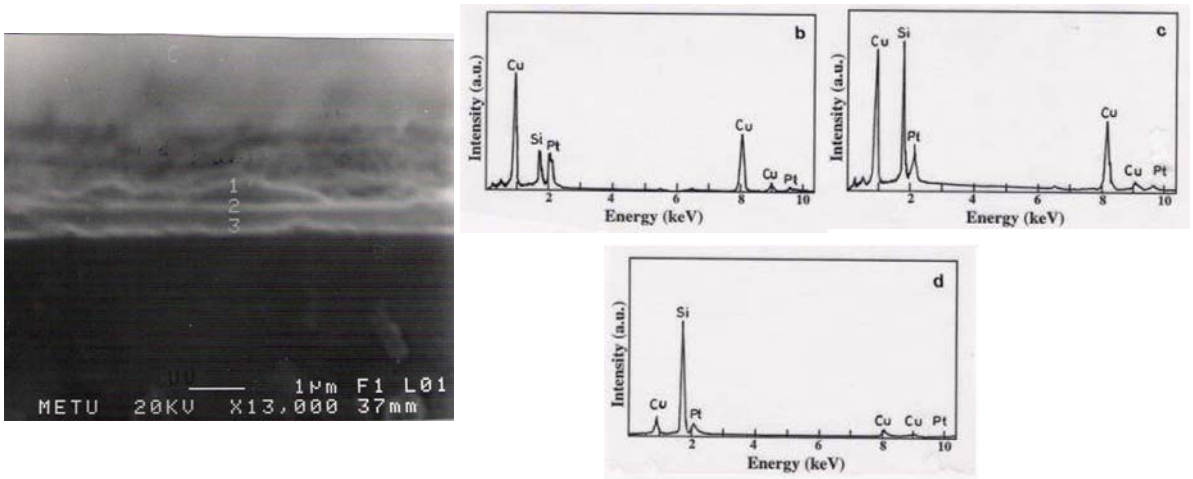

Figure 3.a-) SEM micrograph of 0.68 μm thick Cu film grown on silicon substrate annealed for 3.5 h at 500^0C showing the 1st, 2nd and 3rd layers. EDS spectrum of the same film showing the general elemental distribution which belongs to b-) 1st layer, c-) 2nd layer, d-) 3rd layer.

Table 2 shows thickness variation of $Cu_{0.83}Si_{0.17}$ layer with time and temperature. It can be seen that thicknesses of the $Cu_{0.83}Si_{0.17}$ layers increase with increasing time and temperatures. Meanwhile; thickness measurements; for the samples annealed at 400^0C for 2 and 2.5 h, weren't be able to taken because of poor resolution and we got only three data.

Table 2. Thickness variation in μm with time and temperature of $Cu_{0.83}Si_{0.17}$ layer in Cu / Si system.

Temp.	time				
	2 h	2.5 h	3 h	3.5 h	4 h
400^0C	….	….	0.13	0.15	0.16
500^0C	0.08	0.11	0.16	0.19	0.23
600^0C	0.17	0.24	0.31	0.38	….

The square of measured phase layer thickness of $Cu_{0.83}Si_{0.17}$ versus diffusion time is plotted on a double logarithmic scale for the temperatures; 400^0C, 500^0C and 600^0C as shown in Figure 4. The deviation in the graphic for the sample annealed at 400^0C can be explained by insufficient data. Nonetheless, experimental points were found to lie on a straight line which implies that reactive diffusion obeys parabolic kinetics and can be expressed by $h^2=k.t$; where h is the thickness of $Cu_{0.83}Si_{0.17}$ phase, k is the parabolic rate constant, and t is the diffusion annealing time. Parabolic rate constants were determined by the standard method of least squares analysis together with probable errors as in the following;

$k_1=1.706 \pm 0.06x10^{-14}$ cm^2/s for 400^0C

$k_2=1.972 \pm 0.36x10^{-14}$ cm^2/s for 500^0C

$k_3=7.155 \pm 1.24x10^{-14}$ cm^2/s for 600^0C.

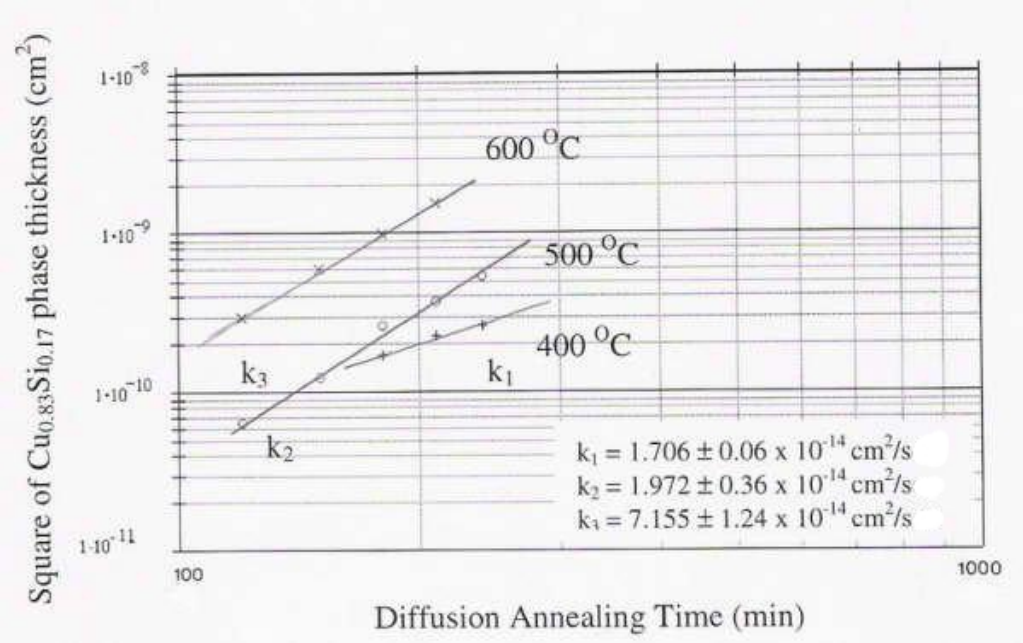

Figure 4. The square of measured phase layer thickness of $Cu_{0.83}Si_{0.17}$ versus annealing time (min) on a double logarithmic scale for 400^0C, 500^0C and 600^0C.

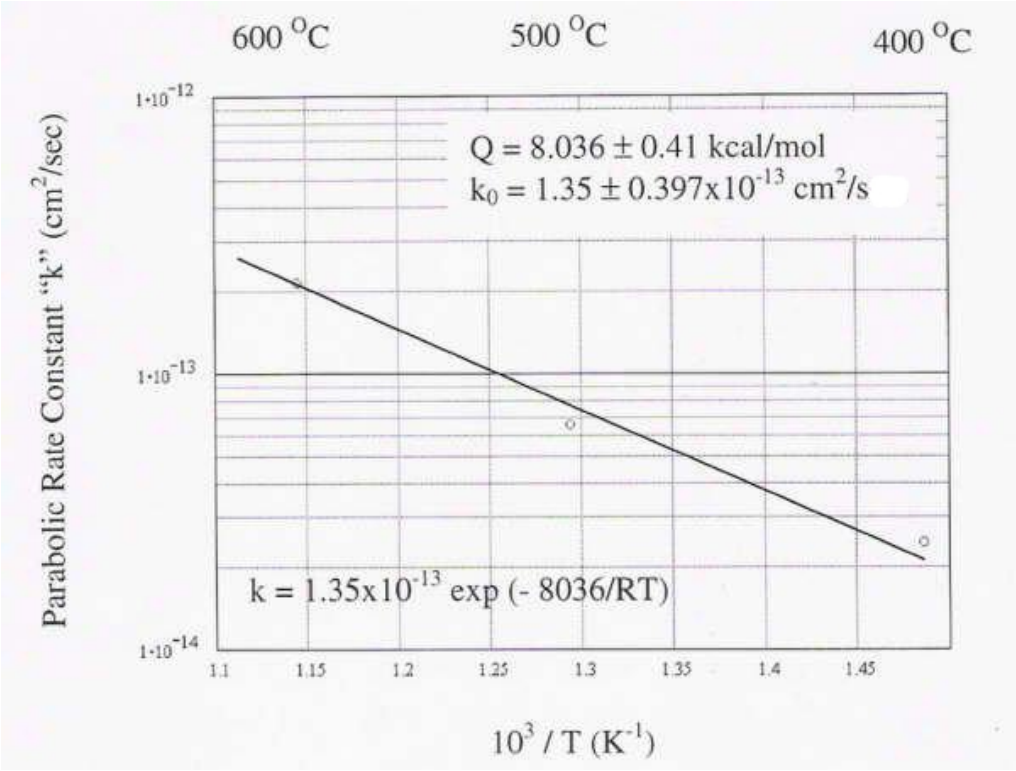

Figure 5. Temperature dependence of the parabolic rate constants for the growth kinetics of the $Cu_{0.83}Si_{0.17}$ phase.

Figure 5 shows the plot of log(k) versus 1/T lie on a straight line, so by using Arrhenius relationship;

$k=k_0\exp(-Q/RT)$ (1)

where k is the rate constant, k_0 is the preexponential factor, Q is the activation energy, and T is the absolute temperature, Q is 8.036 kcal/mol and the preexponential factor, k_0, is $1.35x10^{-13}$ sq cm per sec. As a result; the below equation which is related to the growth kinetic of $Cu_{0.83}Si_{0.17}$ phase can be written as;

$k=1.35x10^{-13}\exp(-8036/RT)$ cm^2/s.

3.2. Cu-(5at%)Nb/SiO_2 System

In order to understand impurity effect, (5at%) Nb was added to copper and silicon substrates were deposited by

Cu-(5at%)Nb films having 0.33μm thickness, and they were annealed at different temperatures and time intervals. Intermetallic phases formed as $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, (Cu, Si)η sequentially at the film-substrate interface were identified from X-Ray diffractograms, SEM micrograph and EDS spectra of Cu-(5at%) Nb films grown on silicon substrates. Those intermetallic phases are listed in Table 3.

X-Ray diffractograms of Cu-(5 at%)Nb films grown on silicon substrate, as-deposited and annealed for 2 h, 2.5 h, 3 h, 3.5 h and 4 h at 500^0C are illustrated in Figure 6. The thickness measurements of $Cu_{0.83}Si_{0.17}$ phase were identified by using SEM micrographs. Thicknesses of the $Cu_{0.83}Si_{0.17}$ layers increase with increasing time and temperatures as shown in Table 4. The square of measured layer thickness of $Cu_{0.83}Si_{0.17}$ versus diffusion annealing time was plotted on a double logarithmic scale for different temperatures, Figure 7. Experimental points were found to lie on a straight line which implies that reactive diffusion obeys parabolic kinetics and can be expressed by $h^2=k.t$. Parabolic rate constants were determined by the standard method of least squares analysis together with probable errors as in the following;

$k_1=3.674 \pm 0.036x10^{-14}$ cm^2/s for 400^0C

$k_2=4.363 \pm 0.107x10^{-14}$ cm^2/s for 500^0C

$k_3=4.947 \pm 1.109x10^{-14}$ cm^2/s for 600^0C.

Table 3. Phases formed during annealing of Cu-Nb(5 at.%) films on SiO_2 substrates for different temperatures and times (constant thickness of 0.330 μm).

No	Heat Treatment	Phases Observed
1	As deposited	Cu, Nb, SiO_2
2	400^0C, t=2 h	$Cu_{0.83}Si_{0.17}$, Cu_4Si, SiO_2
3	400^0C, t=2.5 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, SiO_2
4	400^0C, t=3 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, SiO_2
5	400^0C, t=3.5 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, SiO_2
6	400^0C, t=4 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_5Si, $Nb_5Cu_5Si_4$, SiO_2
7	500^0C, t=2 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, SiO_2
8	500^0C, t=2.5 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, (Cu, Si)η, SiO_2
9	500^0C, t=3 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, SiO_2
10	500^0C, t=3.5 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, (Cu, Si)η, SiO_2
11	500^0C, t=4 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, SiO_2
12	600^0C, t=2 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, SiO_2
13	600^0C, t=2.5 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, SiO_2
14	600^0C, t=3 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, SiO_2
15	600^0C, t=3.5 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, $Nb_5Cu_5Si_4$, SiO_2
16	600^0C, t=4 h	Cu, Nb, $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, (Cu, Si)η, Cu_5Si, SiO_2

Table 4. Thickness variation in μm with time and temperature of $Cu_{0.83}Si_{0.17}$ layer in Cu-(5at%)Nb / Si system.

Temp.	Time				
	2 h	2.5 h	3 h	3.5 h	4 h
400^0C	0.16	0.18	0.20	0.22	0.23
500^0C	0.18	0.19	0.21	0.24	0.26
600^0C	0.19	0.20	0.23	0.26	0.27

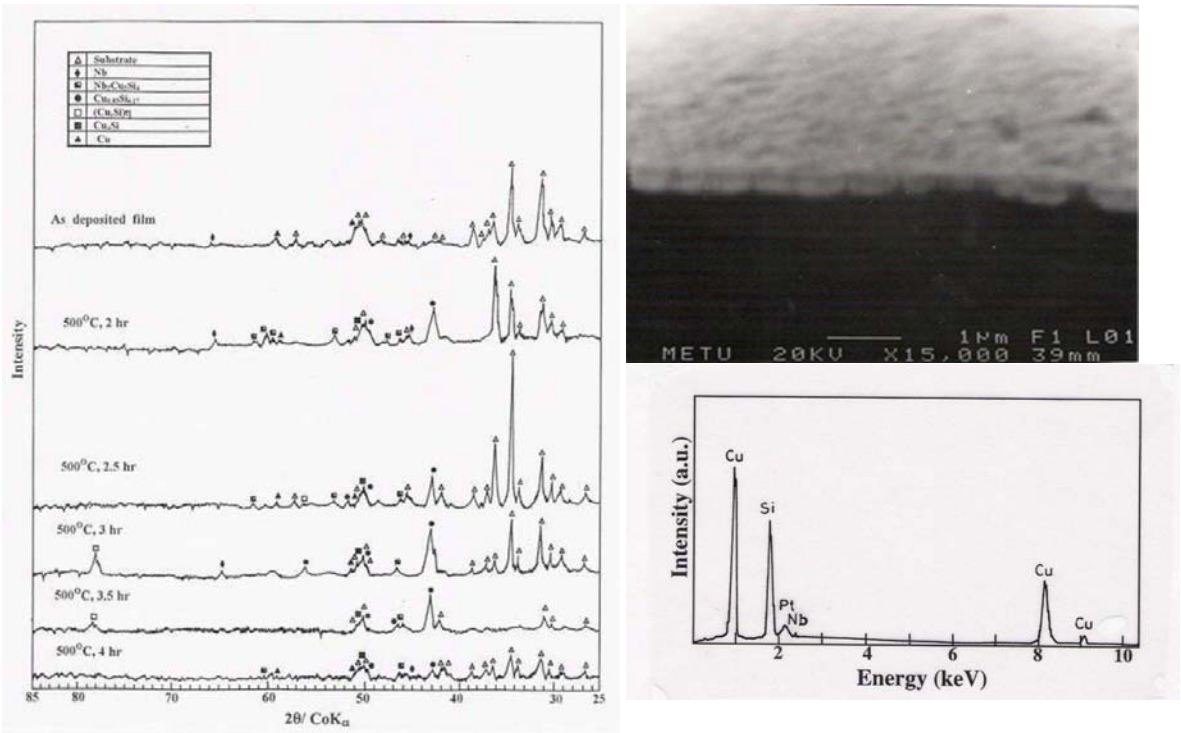

Figure 6. a-) X-Ray diffractograms of Cu-(5 at%)Nb films grown on silicon substrate, as deposited and annealed for 2 h, 2.5 h, 3 h, 3.5 h and 4 h at 500^{0}C., b-) SEM micrograph of 0.33 μm thick Cu film grown on silicon substrate as-deposited; c-) EDS spectrum of the same film.

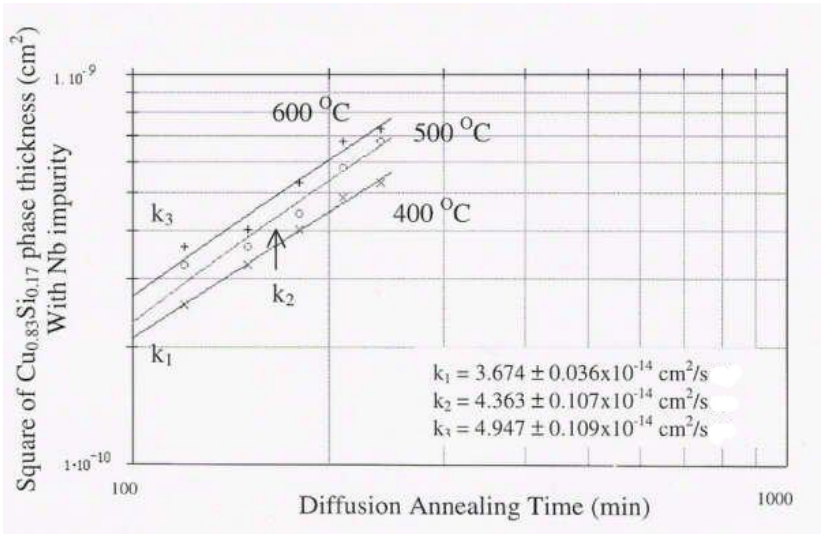

Figure 7. The square $Cu_{0.83}Si_{0.17}$ phase thickness (cm^2) with Nb impurity versus diffusion annealing time (min) on a double logarithmic scale for 400^{0}C, 500^{0}C and 600^{0}C.

Figure 8 shows the plot of log(k) versus 1/T lie on a straight line which obeys Arrhenius relationship.

By using Arrhenius relationship;

$$k=k_0\exp(-Q/RT) \quad (2)$$

where k is the rate constant, k_0 is the preexponential factor, Q is the activation energy, and T is the absolute temperature, the below equation which is related to the growth kinetic of $Cu_{0.83}Si_{0.17}$ phase formed at Cu-(5at%)Nb/Si interface, can be written as:

$$k=1.35x10^{-13}\exp(-1738/RT) \quad (3)$$

After addition of (5at%)Nb to the Cu-Si system; parabolic rate constants increased and activation energy values decreased from the value 8.036 ± 0.41 kcal/mol to the value 1.738 ± 0.056 kcal/mol.

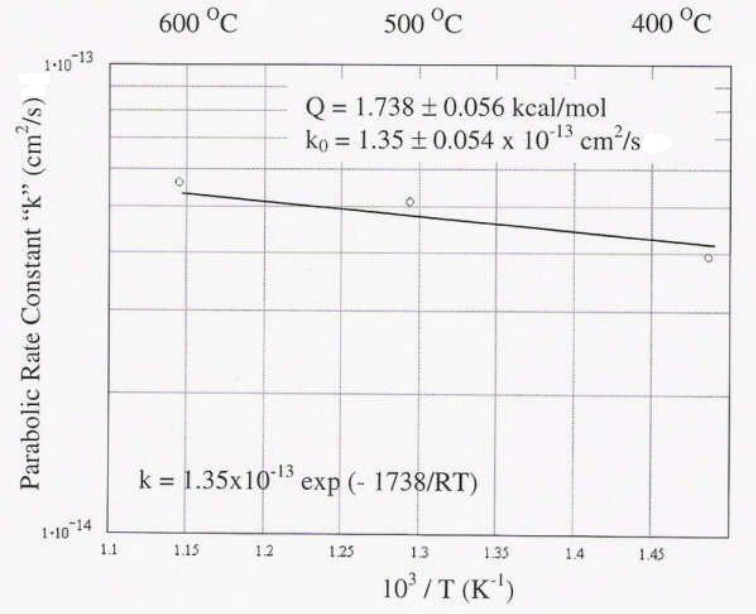

Figure 8. Temperature dependence of the parabolic rate constants for the growth kinetics of $Cu_{0.83}Si_{0.17}$ phase with Nb impurity.

4. CONCLUSIONS

The main conclusions deduced from this work on the intermetallic compound formation at Cu-Si and Cu-(5at%)Nb/Si interfaces may be summarized as follows:

1- XRD, SEM and EDS analysis showed sequential formation of several intermetallic phases at the interfaces. On the contrary, intermetallic phases are simultaneously formed in bulk materials.

2- Intermetallics; $Cu_{0.83}Si_{0.17}$, Cu_4Si, (Cu, Si)η and (Cu, Si)(Si at%21.2), were determined in Cu/Si system. In Cu-(5at%)Nb/Si system, intermetallics; $Cu_{0.83}Si_{0.17}$, Cu_4Si, $Nb_5Cu_5Si_4$, (Cu, Si)η and (Cu, Si)(Si at%21.2), were observed.

3- Experimental results implied that the reactive diffusion obeys parabolic growth kinetics and can be expressed by $h^2=k.t$; where h is the thickness of $Cu_{0.83}Si_{0.17}$ phase, k is the parabolic rate constant, and t is the diffusion annealing time.

4- Parabolic rate constants were determined by the standard method of least squares analysis. From the calculations, Arrhenius type equations can be given as:

For the growth kinetics of $Cu_{0.83}Si_{0.17}$ layer in Cu/Si system;

$k=1.35x10^{-13}exp(-8036/RT)$ cm^2/s

and for the growth kinetics of $Cu_{0.83}Si_{0.17}$ layer in Cu-(5at%)Nb/Si system;

$k=1.35x10^{-13}exp(-1740/RT)$ cm^2/s

5- Parabolic rate constants increase with Nb impurity content and activation energies decrease.

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