RESEARCH ARTICLE

Investigation of Diffusion at the Cu/Hf Interface by X-ray Photoelectron Spectroscopy

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ABSTRACT

The diffusion at the Cu/Hf interface has been investigated *in situ* by the technique of x-ray photoelectron spectroscopy combined with argon ion sputtering. Thick film of hafnium was deposited on a silicon substrate followed by copper. These Cu/Hf samples were annealed at 100, 200, and 300°C for 30 min. The interface width in these samples, as determined from the atomic concentrations, was found to vary linearly with temperature. The interdiffusion coefficients in these samples were determined by the Boltzmann-Matano method. The coefficient is observed to increase with increasing annealing temperature. The Arrhenius plot of the interdiffusion coefficient versus 1/T for 25% atomic concentration of copper was used to determine the activation energy and the pre-exponential factor for this system under the present processing conditions. These values are found to be 0.128 ± 0.003 eV/atom and $3.33\times10^{-14} \pm 1.01\times10^{-14}$ cm^2/s respectively. A comparison with other results indicates that these values depend upon the thickness of the overlayer and the annealing conditions.

Keywords: copper, hafnium, diffusion, x-ray photoelectron spectroscopy, thin films

Introduction

In silicon integrated circuits the interconnection network on the chip is becoming increasingly important for achieving ultra-large scale integration. For this purpose elemental copper has attracted considerable attention because of its physical properties, such as lower electrical resistivity and high electromigration resistance [1]. However, copper has some inherent problems. It oxidizes very easily at a relatively low temperature and cannot form a passive oxide layer [2]. It does not adhere well to many dielectric substrates and is highly reactive with most metals and semiconductors. Copper metallization also has other problems related to both the adequacy of diffusion barrier protecting the fast-diffusing Cu during the subsequent multilevel interconnections and to the high deposition rate and selectivity [3-5]. Copper diffuses rapidly into Si and SiO_2, causing deep-level defects as it contaminates the underlying silicon [6]. In addition to this, a reaction between copper and silicon occurs at temperature as low as 200°C resulting in the formation of the Cu-Si inermetallics. This would cause the premature failure of the electronic devices [7]. The silicon devices must therefore be protected from copper atoms diffusing into the silicon substrate. This can be accomplished either through the preparation of dielectric layers between copper and silicon substrate or by some diffusion barrier. A suitable material to act as a diffusion barrier between copper and silicon has been researched by many groups. In particular, titanium, tungsten, tantalum and their alloys have proved to be effective diffusion barriers because of their high thermal stability [8-10]. Nitrogen purged barriers and amorphous materials (such as TiB_2, Zr–C–N, Ru–Ge, Ti, and Zr-Ni-Ti thin film) [9, 11-15] have also been found to have good barrier properties.

Among the materials investigated for compatible properties hafnium has been found to be particularly interesting [16-20]. Adding hafnium to Cu film is beneficial in retarding the oxidation of copper. Hafnium is negligibly soluble in Cu and has a stronger tendency to oxidize than Cu. It can therefore precipitate out of the Cu matrix to form a passivation layer during annealing in an oxygen atmosphere. Many studies [21-27] have been reported in recent years on the diffusion mechanism of Cu through the diffusion barrier. Ou et al. [28, 29] has investigated the barrier properties of elemental Hf and HfN for possible application as a copper diffusion barrier in the metallization schemes. In the present study, the diffusion of copper overlayer through hafnium has been investigated. Thin films of copper were deposited on a thick film of hafnium over a silicon substrate. The interface was subjected to annealing at different temperatures for a fixed time. The technique of x-ray photoelectron spectroscopy (XPS) combined with argon ion depth profiling has been employed to characterize the sample interfaces. Fick’s second law has been used to determine the interdiffusion coefficient in the Cu/Hf system.

Experimental

The X-ray photoelectron spectroscopic investigation was done by using the Physical Electronics PHI 5100 ESCA system. The source of excitation was the unmonochromatic X-rays obtained from the aluminum anode (energy = 1486.6 eV). For calibration purposes, pure silver, gold, and copper samples were used. The Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks were set to give a binding energy (BE) difference of 848.6 eV. This established the linearity of the BE scale. The Ag $3d_{5/2}$ core level peak was set at 368.2 eV. The full width at half maximum of the Ag $3d_{5/2}$ peak was determined to be 1.8 eV, which gives a measure of the resolution. The high resolution spectra were taken with pass energy of 35.75 eV. A deposition chamber has been attached to the XPS system. The sample can be transferred between these two chambers thus allowing *in situ* characterization of the samples. The deposition chamber is equipped with a quartz crystal monitor. This oscillator has been used to calibrate the rate of deposition of the elements used in this investigation. An Oxford Applied Research electron gun (model EGN4) mounted in the chamber was used for evaporating the metals. Four samples in the form of wire can be mounted onto this gun. The sample to be deposited can be chosen by selecting the appropriate filament. The base pressure in both the deposition chamber and the XPS chamber was better than 2×10^{-9} Torr and rose to about 9×10^{-9} Torr during the deposition. Pure elements of copper and hafnium (of purity 99.99%, Alfa Aesar) have been used in the present investigation.

The silicon substrate was degreased in ethanol and mounted in the chamber. The hafnium film of thickness 800 Å was deposited on this silicon substrate. This was followed by the deposition of about 500 Å film of copper. The samples were annealed at three different temperatures: 100, 200, and 300°C. The annealing time was kept fixed at 30 min for each of these samples. The sample composition was determined as a function of depth by using XPS combined with argon ion sputtering. For this purpose, 4 keV Ar+ ions with ion current of 4.0 $\mu A/cm^2$ were utilized. The sputtering rate was calibrated by separately depositing 200 Å of copper on a hafnium film. The time to sputter the copper away was measured and the sputtering rate was determined to be 2 Å/min. The spectral data in the samples were recorded at a 20 min sputtering time interval. The atomic concentration of copper and hafnium as a function of sputtering time were determined from the area under the peaks. The software MULTIPLAK (Physical Electronics, Inc.) was used for this purpose.

Fick's Second Law:

Diffusion in a binary system consists of analyzing the mobility of atoms as affected by temperature and chemical potential differences across the interface. In such a case the non-steady diffusion process is described by Fick's Second Law. For a one-dimensional diffusion in the binary system, the second law becomes

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x}\right) \tag{1}$$

where c is the atomic concentration of specimen A in B at a given diffusing distance x. D is called the interdiffusion coefficient and generally depends upon the concentration. In such a case, equation (1) can be solved by means of the Boltzmann-Matano analysis. For this analysis a plane is defined with the following criterion:

$$\int_0^d x' dc = 0 \qquad (2)$$

In this equation $x' = x - x_M$, and x_M is the position of the Matano interface, and d is the maximum distance in the binary sample. After the transformation of the variables, the solution to Fick's second law becomes:

$$D(c^*) = -\frac{1}{2t} \cdot \frac{dx}{dc}\bigg|_{C^*} \int_0^{c*} x dc \qquad (3)$$

In this equation, t is the annealing time in seconds. In such an analysis, the error value increases at the ends of the concentration curve. Therefore, the definition of the diffusion coefficient becomes practically impossible when the concentration of one of the components is low. The technique has been found useful in modeling the diffusion through a plane in polycrystalline and monocrystalline materials and in intermetal composites (e. g., Cui et al. [30]). The equation has been used in the present investigation to determine the interdiffusion coefficients for the Cu/Hf samples.

Results and Discussion

The x-ray photoelectron spectra of copper 2p and hafnium 4f core levels were recorded in the high resolution mode as a function of sputter time for the Cu/Hf samples annealed at 100, 200, and 300°C. The spectral data and the atomic concentration plot are shown for the 200°C sample as a representative for all of the samples. Figure 1 shows three spectra for the copper 2p region. Each of the spectrum is characterized by the $2p_{3/2}$ and $2p_{1/2}$ core level peaks at BE values of 932.6 eV and 952.2 eV respectively. These values are in agreement with those reported in the literature for elemental copper [31]. A weak satellite peak appears on the high BE side of each core level peak and is characteristic of the metals. The three spectra shown in this figure correspond respectively at the top of the sample (where the copper concentration is 100%), near the interface region (where the copper concentration is 50%), and towards the end of the interface (where the copper concentration 3%). The strength of the copper signal is observed to continuously decrease across the Cu/Hf interface.

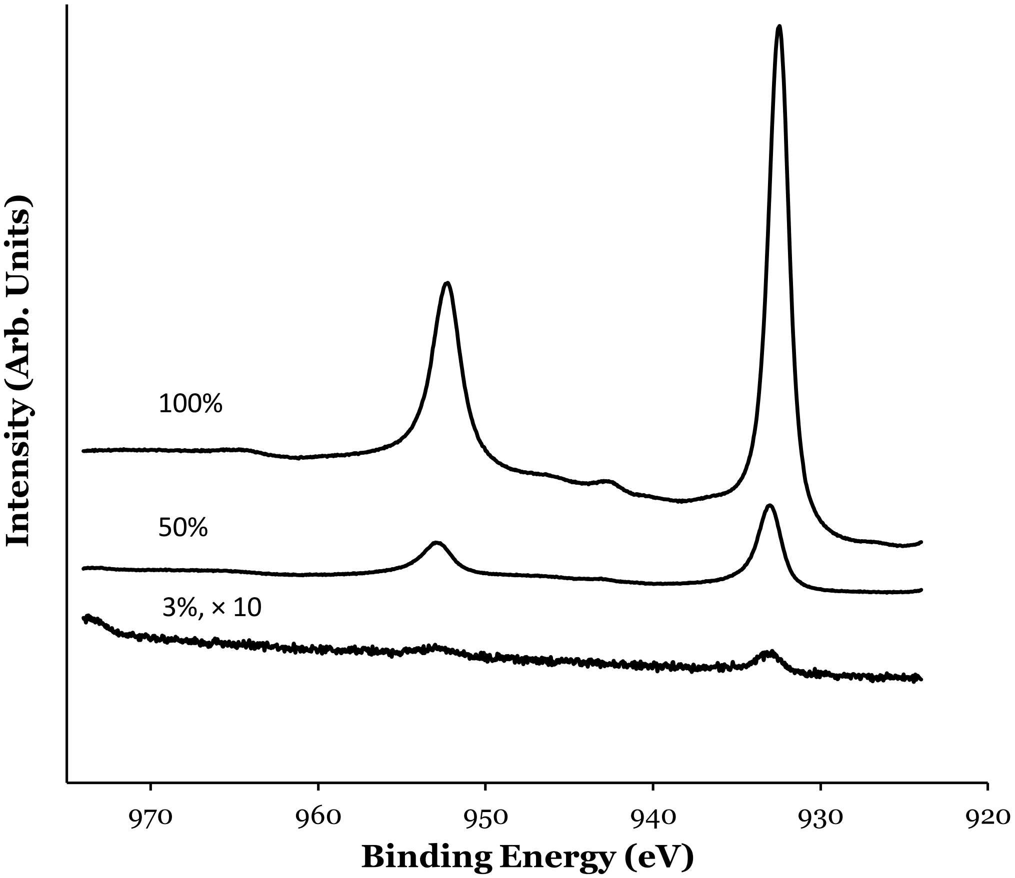

Figure 1: XPS spectra of copper 2p core levels in the 200°C annealed sample. The three spectra correspond to the regions in the sample where the atomic concentration of copper is 100%, 50%, and 3%.

The hafnium 4f spectral peaks for the regions where copper concentrations are 100%, 50% and 3% are shown in Figure 2 for the 200°C annealed sample. The two peaks observed in each spectrum correspond to the $4f_{7/2}$ and $4f_{5/2}$ core levels. Their BEs are determined to be 14.2 eV and 15.9 eV respectively. These values correspond to those for elemental hafnium and are in good agreement with those reported by other researchers [32, 33]. The strength of the hafnium 4f spectral peaks is observed to increase across the interface. The atomic percentages of copper and hafnium were calculated for all of the samples using an equation of the form

$$C_i = (I_i/S_i)/(\Sigma\, I_i/S_i) \qquad (4)$$

where I_i is the area under the peaks and S_i is the respective sensitivity factor. The sensitivity factors for Cu and Hf are taken to be 5.321 and 2.639 respectively [32]. The atomic concentration plot versus the depth (in cm) for the 200°C annealed sample is shown in Figure 3. The sputtering time was converted into the depth scale from the sputtering rate that was determined to be 2 Å/min. The intersection of the atomic concentration data for copper and hafnium is observed to occur at a depth of about 690 cm in this sample. To obtain the dependence of the interface on the annealing temperature, the width of the interface was defined to be the depth difference between the 10% and 90% copper concentrations. This width is plotted as a function of temperature in Figure 4 for the samples under investigation. A straight line fit (shown dashed in the figure) to these data points indicates that the interface width in these samples varies linearly in this temperature range. The results indicate no chemical interaction between the two constituents in this temperature range. No intensity in the 2p region of silicon was observed in these samples. The thickness (800 Å) of the hafnium overlayer used in the present investigation therefore serves as an effective diffusion barrier for copper under the annealing conditions of 300°C and 30 min.

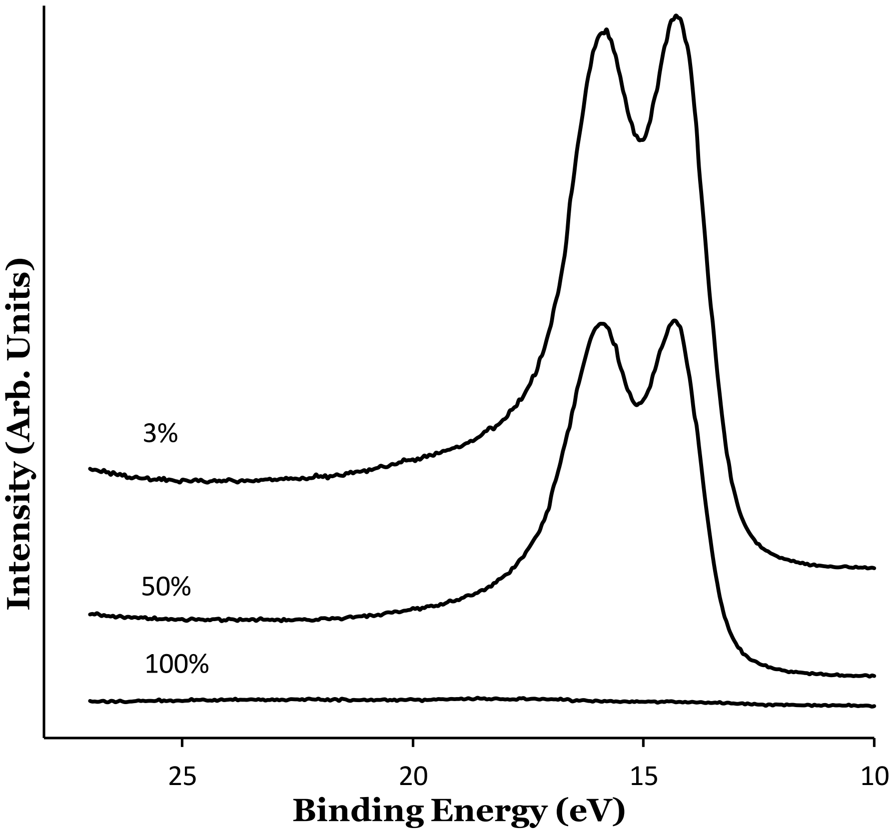

Figure 2: XPS spectra of hafnium 4f core levels in the 200°C annealed sample. The three spectra correspond to the regions in the sample where the atomic concentration of copper is 100%, 50%, and 3%.

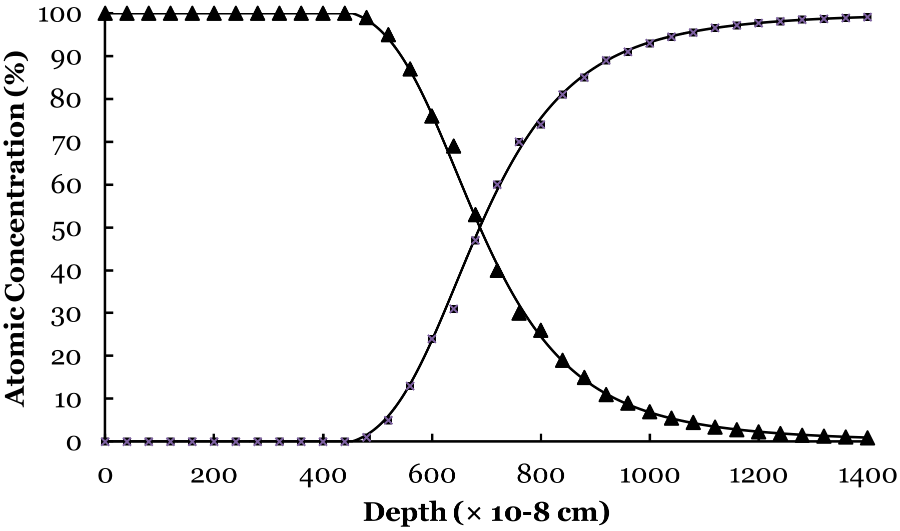

Figure 3: Percentage atomic concentration of copper and hafnium in the 200°C annealed sample as a function of depth. The markers represent the raw data. The triangles represent the copper and the squares represent the hafnium. The lines represent a fit to the raw data.

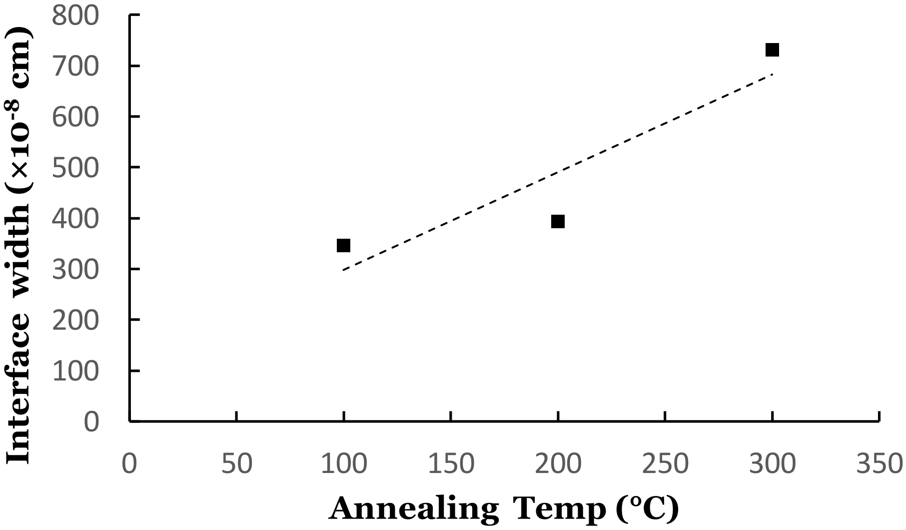

Figure 4: Interface width as a function of annealing temperature. The dashed line is the linear fit to the data. The interface increases linearly with temperature.

The Matano plane across the interface was determined using the conservation of mass criterion. For this purpose, the area under the atomic concentration curve for copper was determined using the trapezoidal rule. This area was determined from the left side and the right side of the atomic concentration curve of Fig. 3. The intersection of these curves marked the Matano plane. The figure has been replotted (shown in Fig. 5) with the depth now referenced to the Matano plane (Eqn. 2) on the ordinate and the atomic concentration of copper on the abscissa. In order to determine the interdiffusion coefficient, the slope was determined at each point on this curve. The trapezoidal rule was used to calculate the integral of equation (3). The interdiffusion coefficients in the three samples have been calculated using equation (3). These coefficients as a function of the copper concentration in the 10-90% range are plotted in Figures 6 (a-c). The diffusion coefficient is seen to increase with the temperature in these samples. The diffusion coefficients obtained in the present study for 25% copper concentration in the samples are given in Table 1. Also included in this table are the results on the diffusion coefficients of bulk copper obtained by Kuper et al. [34]. They have used tracer techniques and have studied eight different samples. These samples were annealed for periods of 8 to 48 hours in a temperature range of 660-1062°C. The comparison with the present investigation therefore suggests that the diffusion coefficient depends, among other things, upon the thickness of the overlayer and the annealing conditions.

Table 1: Interdiffusion coefficient for the Cu/Hf samples at 25% atomic concentration of copper. The results (*) from Kuper et al. [34] are also included

Annealing Temperature (°C)	Interdiffusion Coefficient (cm^2/s)
100	$7.29\times10^{-16} \pm 1.40\times10^{-16}$
200	$9.68\times10^{-16} \pm 2.22\times10^{-16}$
300	$31.8\times10^{-16} \pm 6.49\times10^{-16}$
(*) 660-1062	(*) $4.12\times10^{-9} - 2.53\times10^{-12}$

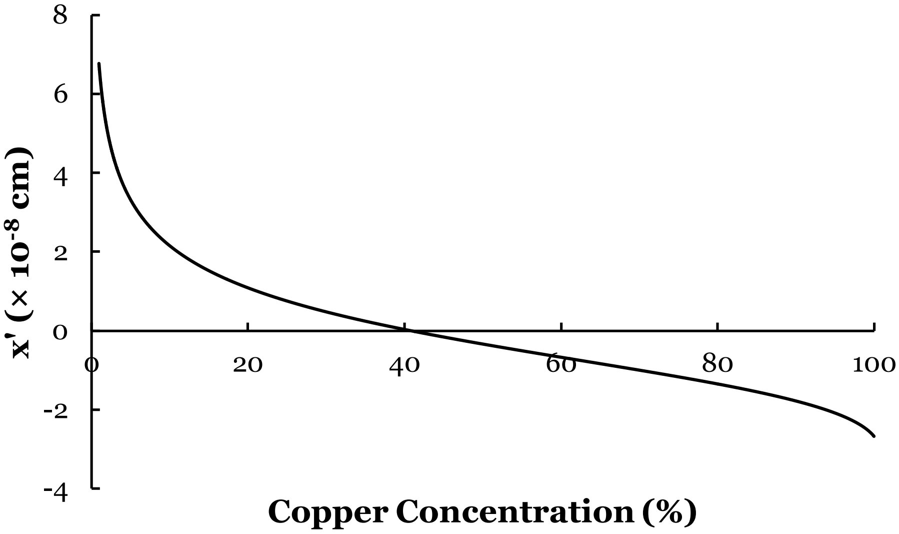

Figure 5: Percentage atomic concentration of copper as a function of depth referenced to the Matano plane, as determined using equation (2). The interdiffusion coefficient has been calculated from this figure.

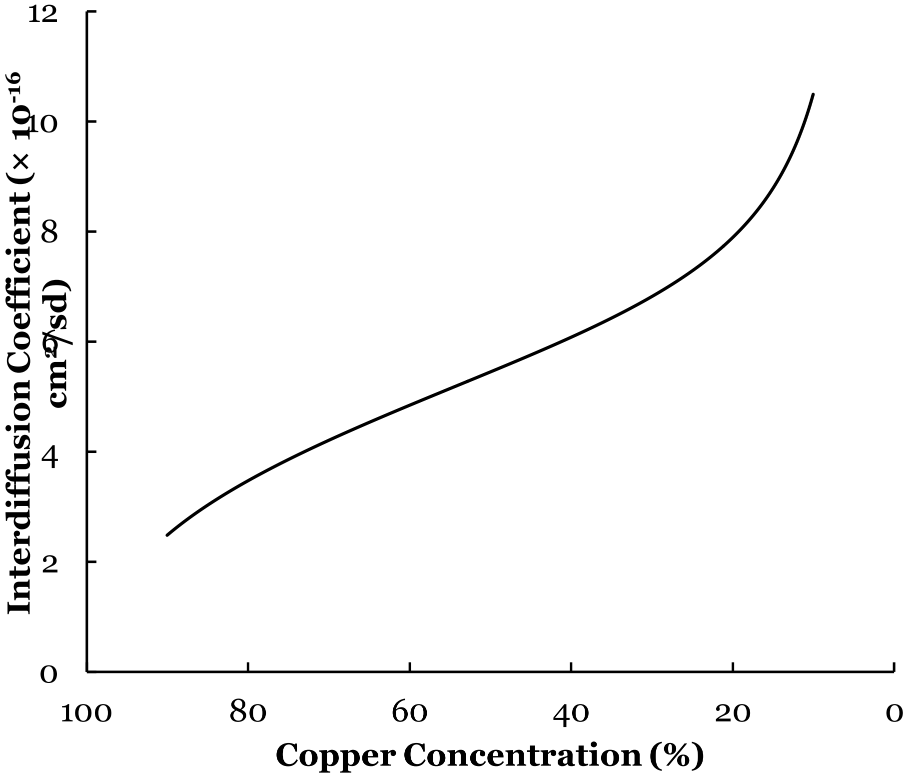

Figure 6(a): Interdiffusion coefficient as a function of atomic concentration of copper in the 100°C annealed sample calculated using equation (3).

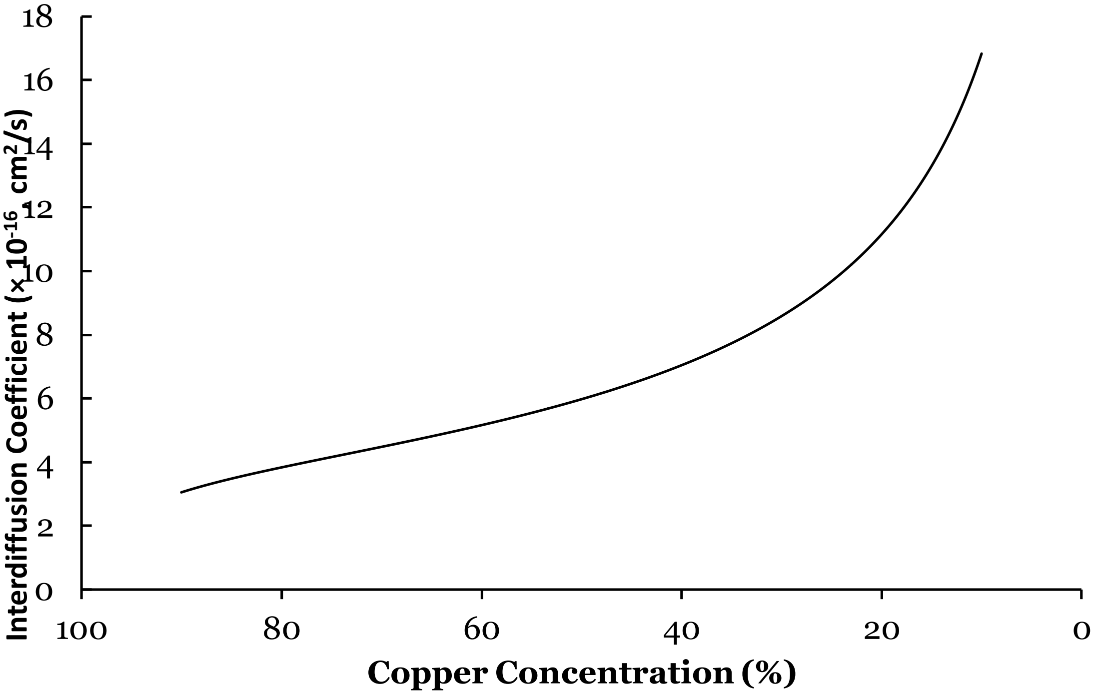

Figure 6(b): Interdiffusion coefficient as a function of atomic concentration of copper in the 200°C annealed sample calculated using equation (3).

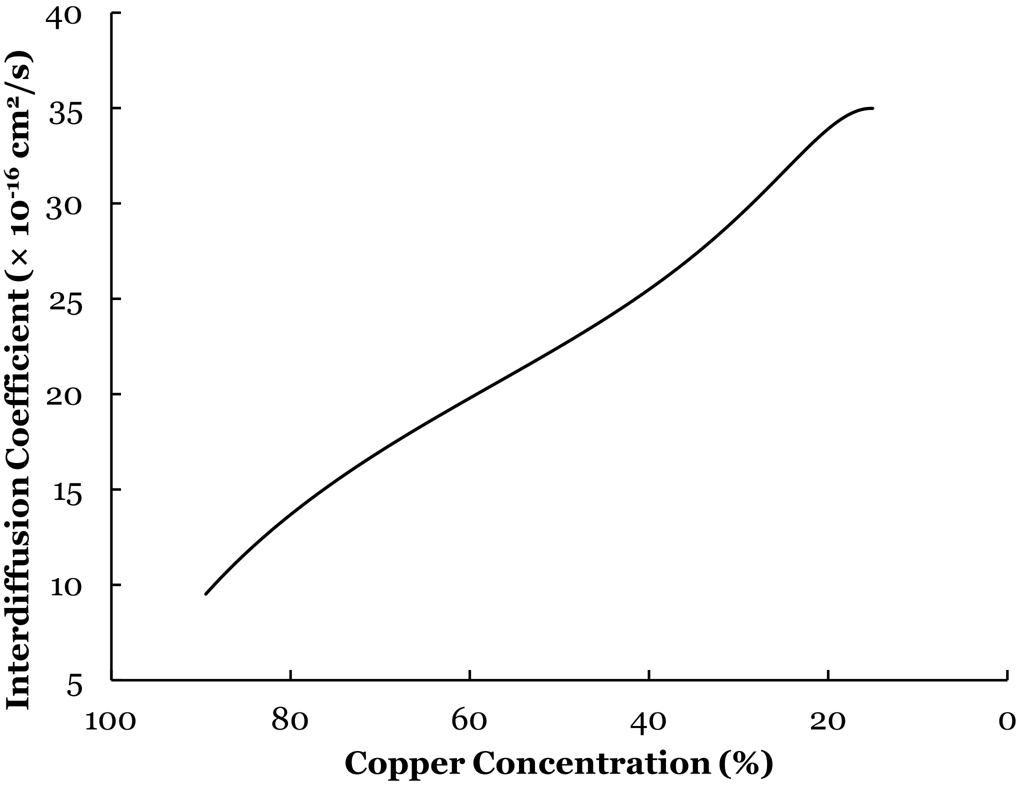

Figure 6(c): Interdiffusion coefficient as a function of atomic concentration of copper in the 300°C annealed sample calculated using equation (3).

The Cu/Hf system has not been studied extensively. Ou et al. [28, 29] have investigated the barrier properties of Cu-Hf system. In their study, no interfacial reaction between Hf and Cu is observed until the annealing temperature of 550°C and with an annealing time of 30 min. Copper was observed to diffuse through the 50 nm thick Hf layer and react with the silicon substrate to form copper silicide when the annealing temperature was set at 600°C for 30 min. The hafnium layer failed to act as a diffusion barrier under these conditions. The thermal stabilities of the Cu/Hf interface were found to be improved by the nitrogen incorporation. The formation of HfN and deposition of multilayered amorphous HfN layers were observed to enhance the barrier properties for annealing temperature of up to 650°C and annealing time of 30 min. The results of the present investigation that no chemical interaction occurs between copper and hafnium and that the diffusion coefficient increases with increasing annealing temperature are consistent with the results obtained by Ou et al. The structural changes and electrical properties of Cu/Hf thin films have been investigated by Fang and Chen [35]. The films were annealed in a temperature range from 200-600°C for 30 min in an oxygen atmosphere. At elevated temperatures the hafnium was observed to get oxidized. High hafnium content favored the best passivation behavior but at the cost of a higher electrical resistivity. More studies on the Cu/Hf system are needed to optimize the fabrication of hafnium based devices.

The diffusion coefficient is an important parameter for describing the diffusion process. Over a wide range of temperature, experimentally measured diffusion coefficients often fit the Arrhenius relation:

$$D = D_0 \exp(-E_a/kT) \qquad (5)$$

where k is the Boltzmann constant, T is the absolute temperature, D_0 is the pre-exponential factor, and E_a is the activation energy. Both E_a and D_0 are independent of the temperature. They depend on the identity of the diffusing element and the composition of the matrix crystal. External factors such as forces and pressure can also affect E_a and D_0. A plot of ln(D) vs 1/T will be straight line. The activation energy can be determined from the slope of this line. The intercept of this line will give the pre-exponential factor. A plot of ln(D) vs 1/T for the 25% copper in the samples is shown in Figure 7. A straight line fit to these data points (shown as a dashed line in this figure) has been used to determine the activation energy and the pre-exponential factor. These values are listed in Table 2. The values obtained by Kuper et al. [34] are also listed in this table. The pre-exponential factor as calculated by Zener's theory [Ref. 5 in Kuper et al.] is also listed in this table.

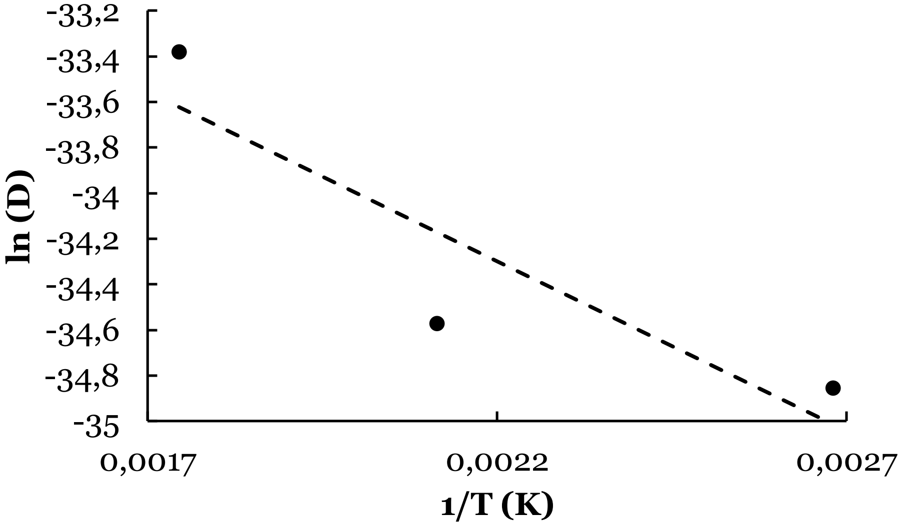

Figure 7: Arrhenius plot of the ln(D) vs 1/T. The dashed line is a linear fit to the data. The activation energy and the pre-exponential factor have been determined from the slope and the intercept of this line.

Table 2: Results from Arrhenius plot of Fig. 7. The results (*) from Kuper et al. [34] and theoretical value (**) from Ref. [5] in Kuper et al. are also included

Pre-exponential Factor, D_0 (cm^2/s)	Activation Energy, E_a (eV/atom)
$3.33\times10^{-14} \pm 1.01\times10^{-14}$	0.128 ± 0.003
(*) 0.128	(*) 2.00
(**) 0.28	

Several factors affect the inter-diffusion: grain boundaries, mono- and di-vacancies, crystalline and non-crystalline nature of the films, the structure of the films, relatively high concentration of uncontrolled impurities, stress at the interface, poor thermal stabilities, etc. [36] In this study the depositions of the hafnium and copper films were done at room temperature. The influence of the amorphous nature of the films on the diffusion coefficients and the Arrhenius parameters cannot be ruled out. In addition, different factors such as information depth, ion beam inhomogeneity, original and beam induced roughness, knock-on and atomic mixing effects, preferential sputtering, enhanced atomic migration etc. influence the depth resolution in sputtering techniques (e. g., see [37]). These uncertainties can be reduced by performing the depth profiling of the samples by non-destructive technique, such as Rutherford Backscattering Spectrometry. In the present investigation all of the samples were subjected to identical sputtering conditions. Therefore, the sputtering technique is expected to affect all of the samples in a similar manner.

In conclusion, the Cu/Hf interface has been investigated by the technique of x-ray photoelectron spectroscopy. The samples were annealed for 30 min at three different temperatures. The depth profiling was performed by argon ion beam sputtering. The interface width was found to vary linearly with the temperature. The thickness of the hafnium overlayer was observed to serve as an effective barrier for copper. The Boltzmann-Matano method was used to determine the interdiffusion coefficients in these samples. The coefficient was observed to increase with increasing temperature. The Arrhenius plot of the interdiffusion coefficient and the temperature for the 25% atomic concentration of copper was used to determine the activation energy and the pre-exponential factor in this system. These values are found to be 0.128 ± 0.003 eV/atom and $3.33\times10^{-14} \pm 1.01\times10^{-14}$ cm^2/s respectively and depend upon the processing conditions.

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