

Diffusion of Implanted Metals in Tantalum Silicide

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Abstract. In this paper we presented the diffusion behavior of ³⁹K, ⁴⁰Ca, ⁴⁸Ti, ⁵¹V, ⁵²Cr and ⁵⁵Mn ion implanted into 500 nm TaSi₂ layers co-sputtered on silicon. The samples were annealed at temperatures ranging from 300-1000°C for 30 minutes. The transition elements studied (⁴⁸Ti, ⁵¹V, ⁵²Cr and ⁵⁵Mn) show very similar diffusion behavior. SIMS profiles show no movement for these transition metal elements for the 300 and 500°C annealed samples, some diffusion at 700°C, and significant diffusion at 900 and 1000°C For Alkali or alkaline metals such as ³⁸K and ⁴⁰Ca, SIMS depth profiles show more limited. Ti, V, Cr, and Mn diffuse faster than K and Ca in this silicide

Introduction

Silicides are compounds of silicon with more electropositive elements in the periodic table, and are referred to as intermetallic materials, with behavior similar to metals. In recent years, transition-metal silicides attracted the attention of many researchers because of their useful applications in silicon integrated circuits (ICs). Silicides are used as conductors in ICs because of properties such as corrosion resistance, stability at high temperature, and lower electrical resistivity. Researchers used many techniques to produce these materials, such as powder metallurgical techniques in 1950s through 1960s [1, 2]. Currently, there are two main methods which have been used to form silicides. In the first method, the metal is deposited on a Si substrate, which is then annealed to react the Si and metal [3]. The second method is sputtering of separate metal and Si targets or a composite metal-silicon target to form a silicide layer on top of the substrate [4, 5]. The second method was used to form the silicide layers on top of silicon substrate for this study.

There are several works done on diffusion in silicide. Wittmer et al [6] studied the low-temperature diffusion of dopant atoms in silicon during interfacial silicide formation. They noted that diffusion enhancement occurs only during interfacial formation of near-noble- silicides such as PtSi, Pd₂Si and NiSi but not refractory-metal silicides such as TiSi, TiSi₂, VSi₂ and TaSi₂. Myers et al [7] studied the implantation-formed cavities and boron-silicide precipitates as strong segregation getterings for transition metals. They reported that both appear to be promising. Maex et al [8] investigated the stability of the doped Si with respect to silicides. They reported that high concentration of As-doped and B-doped Si are unstable underneath an overlaying silicide layer. In this paper we will study the diffusion behavior of K, Ca, Ti, V, Cr and Mn ion implanted into 500 nm TaSi₂. Secondary ion mass spectrometry, SIMS, is used to obtain the concentration-depth profiles after thermal annealing.

Experimental Procedures

The substrate material is (100) silicon and the silicide thin film (TaSi₂) is prepared on top of it. The silicide layer is polycrystalline and about 500 nm thick. Ion implantation has been used to implant ³⁹K, ⁴⁰Ca, ⁴⁸Ti, ⁵¹V, ⁵²Cr and ⁵⁵Mn ions into the silicide layer. The implantation energy varies over 70-180 keV. Thermal annealing was carried out for the implanted samples at temperatures from

300°C to 1000°C, for 30 minutes each. The annealing procedures were done using a Lindberg furnace with a long quartz tube. The furnace was heated to a desired temperature, then the quartz tube with the sample was placed in the center of the furnace. The annealing temperature was controlled to within $\pm 1^\circ\text{C}$. A constant flow of high purity (99.999 %) Ar gas was maintained through the quartz tube during the annealing process. After completion of the anneal process, the quartz tube was removed from the furnace immediately and the sample was cooled to room temperature within the flow of argon gas.

Secondary Ion Mass Spectrometry (SIMS) was used to obtain depth profiles of the elements of interest. The SIMS characterization was carried out at the UCF/Agere Materials Characterization Facility with a CAMECA IMS-3f using 100 nA O_2^+ primary beam at a source potential of 10 kV, an impact energy of 5.5 keV and impact angle of 40° from normal. The focused primary beam of oxygen ions was rastered over $200 \times 200 \mu\text{m}^2$ or $250 \times 250 \mu\text{m}^2$ areas, with detection of ions from an area of 60 μm diameter at the center of the raster. The sputtering rate was approximately 0.6 nm/s. The depth scale was established for each profile by measuring the crater depth with a stylus profilometer (Sloan Dektak IIA). The concentration was calibrated with the implantation dosages of the as implanted samples and the measured erosion rate.

Results and Discussions

In figure 1, we present the depth profiles of ^{39}K and ^{40}Ca implanted into 500 nm TaSi_2 with implantation energy of 150 keV. Figure 1(a) shows SIMS profiles for ^{39}K , 1×10^{14} ions/ cm^2 , as-implanted and annealed at 700, 900 and 1000°C for 30 minutes. Depth profiles show almost no diffusion for 700 and 900°C, but for the 1000°C annealed sample, ^{39}K started to diffuse into the silicide layer. The data indicate that ^{39}K is relatively immobile in silicide. Figure 1 (b) shows somewhat different depth profiles for ^{40}Ca , 1×10^{14} ions/ cm^2 , implanted into TaSi_2 . The as-implanted and 700°C annealed samples show the same depth profile, which means there is no diffusion for ^{40}Ca ions up to 700°C. SIMS profiles for the 900 and 1000 °C annealed samples show ^{40}Ca movement into the silicide. For 900°C the Ca diffused to about 275 nm and then decreases rapidly, and for the 1000°C annealed sample we noticed that Ca diffused through the entire silicide layer.

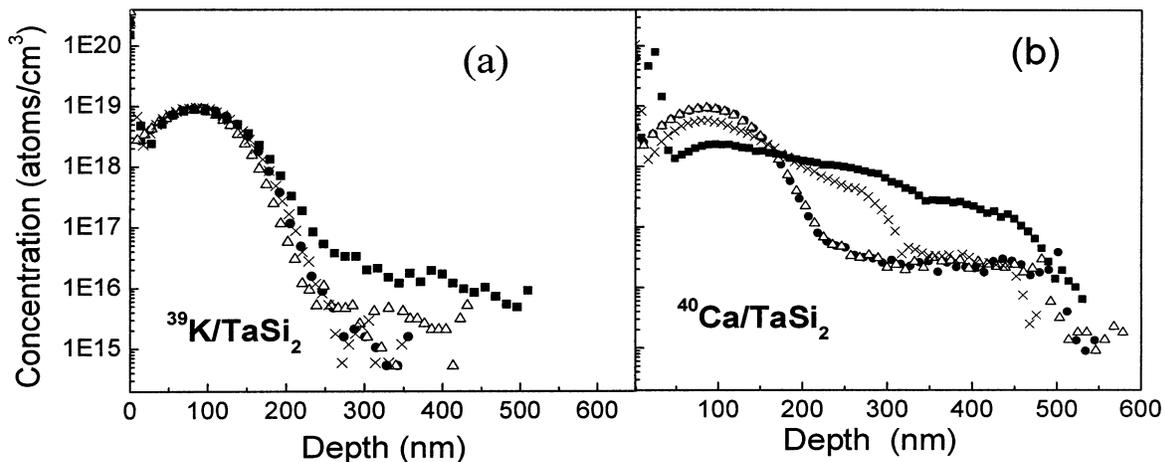


Figure 1. SIMS depth profiles of : (a) ^{39}K (150 keV, $1\text{E}14$ ions/ cm^2) and (b) ^{40}Ca (150 keV, $1\text{E}14$ ions/ cm^2). (● As-implanted, Δ 700°C, \times 900°C, \blacksquare 1000°C).

Figure 2 shows the depth profiles for ^{48}Ti and ^{51}V both with the same dosage of 1×10^{14} ions/cm 2 and the same implantation energy of 150 keV. Figure 2(a) shows ^{48}Ti SIMS profiles for samples as-implanted and annealed at 300-1000°C for 30 minutes. As implanted, 300 and 500°C depth profiles show no movement of the implants. At 700 °C we detect diffusion in the silicide layer. At higher temperatures, 900 and 1000°C, ^{48}Ti displays a flat concentration profile in the silicide layer. At 500 nm depth, the concentration profile shows a step and this is due to the differences in the solubility and diffusivity of Ti in silicide and in silicon. From figure 2(b), we can see that the ^{51}V has a diffusion behavior similar to ^{48}Ti . For as-implanted, 300 and 500°C, ^{51}V does not show any movement inside the silicide layer but at 700°C we detect diffusion behavior at 200 nm depth. At 900 and 1000°C, the depth profiles show complete diffusion of V in silicide.

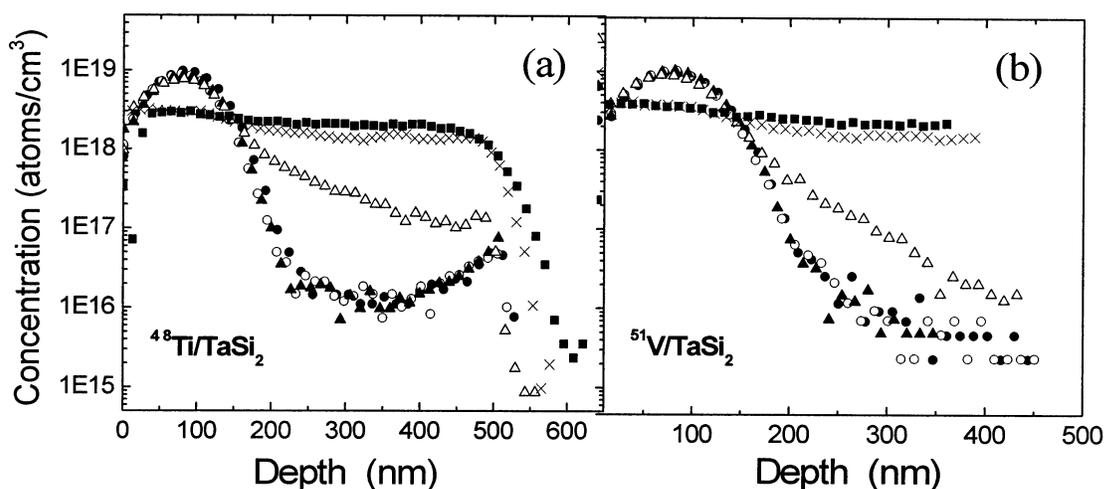


Figure 2. SIMS depth profiles of : (a) ^{48}Ti (150 keV, $1\text{E}14$ ions/cm 2) and (b) ^{51}V (150 keV, $1\text{E}14$ ions/cm 2). (● As-implanted, ○ 300°C, ▲ 500°C, △ 700°C, × 900°C, ■ 1000°C).

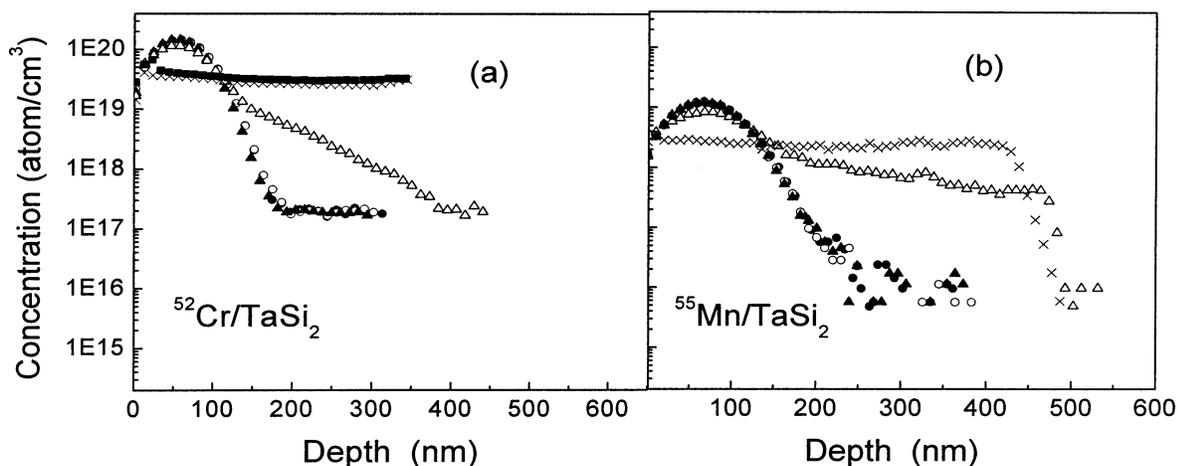


Figure 3. SIMS depth profiles of (a) ^{52}Cr (120 keV, $1.1\text{E}15$ ions/cm 2) and (b) ^{55}Mn (150 keV, $1.1\text{E}14$ ions/cm 2). (● As-implanted, ○ 300°C, ▲ 500°C, △ 700°C, × 900°C, ■ 1000°C).

Figure 3 shows concentration profile of ^{52}Cr , 1.1×10^{15} ions/cm², and ^{55}Mn , 1.1×10^{14} atoms/cm², implanted into TaSi₂ with implantation energies of 120 and 150 KeV respectively. As shown in Figure 3(a) and 3(b), ^{52}Cr and ^{55}Mn depth profiles show no movements of the implanted ions after 300 and 500°C anneal. Movements of ^{52}Cr ions begin to be observed for the 700°C-annealed sample at 150 nm depth and beyond. After 900°C annealing, ^{52}Cr and ^{55}Mn ions show flat concentration profile inside the silicide layer.

Conclusion

We present, for the first time, SIMS concentration profiles of six metal ions (K, Ca, Ti, V, Cr, and Mn) implanted into TaSi₂ and annealed at temperatures between 300°C and 1000°C. We found that the four transition metal ions (Ti, V, Cr, and Mn) show no movements after 500°C anneal and start to diffuse into the bulk after 700°C anneal. After 900°C anneal, the concentration profiles are almost flat. For K and Ca, the concentration profiles at 700°C anneal still remain the same as that of the as-implanted sample.

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