

## A MODEL FOR TITANIUM SILICIDE FILM GROWTH

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### ABSTRACT

*A physical model has been developed that describes the formation of titanium silicide from deposited titanium films on silicon substrates during furnace annealing. The model for  $TiSi_2$  formation consists of set of diffusion-reaction equations and a set of equations for the mechanical behavior of the materials present. Some of the parameters for the model have been obtained from data published in the literature. A one-dimensional computer implementation of the model has been developed that shows the time evolution of the growing layers and their constituents. This is useful for understanding the mechanisms that determine the relative thicknesses of various layers, like  $TiSi_2$  and  $TiN$ , that grow at different temperatures during  $N_2$  annealing.*

### INTRODUCTION

Silicide films have received much recent attention because of their practical applications for VLSI technologies. Titanium silicide is among the most common silicides employed in the semiconductor industry because it can be self-aligned, has low resistivity, and is stable at temperatures consistent with device fabrication processes. Previous studies have been directed at understanding and modeling the titanium-silicon reaction [1-2], with some disagreement as to the activation energy for this reaction. In applications where the self-aligning feature is desired, the reaction typically occurs in the presence of a reactive ambient, usually nitrogen. For titanium deposited on a clean silicon substrate and heated in the presence of nitrogen, titanium nitride begins forming at the surface while titanium silicide forms at the Ti-Si interface. The reactions proceed until the growth fronts come together, where they cease unless there is sufficient thermal activation to begin converting the  $TiSi_2$  to  $TiN$ . A physical model has been developed that describes the formation of titanium silicide for a deposited titanium film on a

lightly doped silicon substrate during furnace annealing in either inert or nitriding ambients.

### EXPERIMENTAL PROCEDURE

Titanium films were deposited by evaporation on lightly doped, precleaned silicon substrates and on silicon wafers in which 200 nm of oxide had been thermally grown. The wafers were annealed in either forming gas, or argon at temperatures ranging from 500°C to 800°C. XPS and/or Auger depth profile analysis was performed in order to determine the elemental composition of the films. TEM cross section micrographs were obtained for certain samples to aid in determining the thicknesses of the individual phases present.

### METALLURGICAL ASPECTS

Some discussion in the literature has been devoted to describing the silicidation reaction [3] which occurs when a metal is brought in contact with the surface of silicon and heated to temperatures high enough so that interdiffusion can take place. In the case of the Ti-Si reaction couple, silicon is the dominant diffusing species. As the silicon begins reacting with the titanium, nucleation and growth of a silicide phase or phases occurs, which effectively isolate the substrate from the remaining titanium film, and through which diffusion must occur in order for the reaction to continue. The nucleation process may be described as nonclassical in the sense that the gradient energy, arising from the steep concentration gradient at the interface, plays a significant role in the nucleation of the silicide phase(s). Because  $TiSi$  and  $TiSi_2$  are both line compounds, the equilibrium solid solubility of silicon in these phases is very low. The solid solubility of Si in the metastable (C49) phase of  $TiSi_2$  is not known, however, because the (C49) phase is typically found to form first and then convert to the stable (C54) phase, the silicon

solubility in this metastable phase is perhaps the more relevant quantity. The smaller grain size and more heavily-faulted microstructure, typical of the (C49) phase, may be associated with a higher silicon solubility and diffusivity than in the stable equilibrium phase. Finally, because the system under consideration is not in equilibrium during the critical nucleation and growth period, many of the parameters required for modeling this reaction must be obtained through empirical methods.

## TITANIUM SILICIDE MODEL

### Neutral Ambient Furnace Annealing

In inert or vacuum ambients, silicon is assumed to enter the growing  $TiSi_2$  layer at the substrate interface, diffuse through the silicide, and then react with either Ti to form  $TiSi$ , or with  $TiSi$  to form additional  $TiSi_2$ . Many of the details of this picture are uncertain. The assumptions that have been used for the current model are as follows:

- 1) The silicon diffusion rate depends in a simple way on the local material composition; i.e.,  $D_{Si} = F_{TiSi_2} D_{Si}^0$  where  $F_{TiSi_2}$  is the local fraction of  $TiSi_2$  and  $D_{Si}^0$  is the diffusivity of silicon in pure  $TiSi_2$ .
- 2) The reactions that form  $TiSi$  and  $TiSi_2$  obey law of mass action and are irreversible. Both of the above reactions are accompanied by volume changes. Modeling of this effect is discussed below. All of the details of nucleation and grain growth are ignored in this model.
- 3) The rate of consumption of the substrate is taken to be proportional to the flux of silicon into the silicide. The Si concentration at the substrate interface is assumed to quickly reach a stable equilibrium value  $C_{Si}^*$ . The mechanisms that dominate the initial stages of silicide growth and silicon concentration stabilization are therefore assumed to have a small effect. This may be true for furnace annealing, but may not be true for rapid thermal annealing, where the time required for the the reduction of the interfacial oxide may be significant with respect to the overall reaction time.

All of the above considerations are summarized in the following model equations:

$$\frac{\partial C_{Si}}{\partial t} + \nabla \cdot (\vec{v} C_{Si}) = \nabla \cdot (D_{Si} \nabla C_{Si}) - k_1 C_{Si} C_{Ti} - k_2 C_{Si} C_{TiSi} \quad (1)$$

$$C_{Si} = C_{Si}^* \quad (2)$$

$$\vec{v} = V_{Si} D_{Si} (\nabla C_{Si} \cdot \vec{n}) \vec{n}, \quad (3)$$

where  $C_{Si}$  is the concentration of silicon,  $\vec{v}$  is the velocity field of the nondiffusing materials that are present,  $k_1$  is the forward reaction rate for  $Si + Ti \rightarrow TiSi$ ,  $k_2$  is the rate for  $Si + TiSi \rightarrow TiSi_2$ ,  $V_{Si}$  is the volume occupied by a silicon atom in the substrate, and  $\vec{n}$  is a unit normal at the substrate interface. Equations (2) and (3) apply only at the silicide-substrate interface. All other boundaries are taken to be reflecting for silicon. The diffusivity of silicon in all materials except  $TiSi_2$  is regarded as insignificant compared with other processes that may be occurring. The diffusion term on the right side of equation (1) is evaluated in a frame that comoves with the  $TiSi_2$ .

The other species present are treated in the same way as silicon, except that they are assumed to be nondiffusers. The corresponding equations for Ti,  $TiSi$ , and  $TiSi_2$  are

$$\frac{\partial C_{Ti}}{\partial t} + \nabla \cdot (\vec{v} C_{Ti}) = -k_1 C_{Si} C_{Ti} \quad (4)$$

$$\frac{\partial C_{TiSi}}{\partial t} + \nabla \cdot (\vec{v} C_{TiSi}) = k_1 C_{Si} C_{Ti} - k_2 C_{Si} C_{TiSi} \quad (5)$$

$$\frac{\partial C_{TiSi_2}}{\partial t} + \nabla \cdot (\vec{v} C_{TiSi_2}) = k_2 C_{Si} C_{TiSi} \quad (6)$$

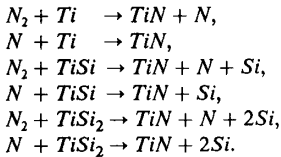
The above model equations are not complete. Additional equations are required for the velocity field  $\vec{v}$ . If  $V_x$  is defined to be the average volume occupied by species x (by analogy with  $V_{Si}$ ), then by definition,  $\sum V_x C_x = 1$ , where  $C_x$  is the concentration of x. If equations (1) and (4)-(6) for each species are multiplied by the corresponding values  $V_x$  and then summed, it follows that

$$\nabla \cdot \vec{v} = V_{Si} \nabla \cdot (D_{Si} \nabla C_{Si}) + k_1 (V_{TiSi} - V_{Si} - V_{Ti}) C_{Si} C_{Ti} + k_2 (V_{TiSi_2} - V_{Si} - V_{TiSi}) C_{Si} C_{TiSi} \quad (7)$$

It is known experimentally that  $V_{TiSi} < V_{Si} + V_{Ti}$  and  $V_{TiSi_2} < V_{Si} + V_{TiSi}$ . Equation (7) therefore asserts that the film sees swelling due to the influx of silicon and shrinkage relative to the original reactant volumes. The above equations are now adequate to describe one-dimensional  $TiSi_2$  growth at thermal equilibrium. In two dimensions, however, it is also necessary to solve the momentum equation. One must then have some knowledge about the behavior of the materials at the processing temperature; e.g., that the materials are linear elastic solids with mechanical properties that depend on composition.

### Annealing in $N_2$ or $NH_3$

Nitriding ambients modify the basic picture described above. For ambients containing nitrogen, a surface TiN layer forms that competes with the growth of  $TiSi_2$  from the substrate. In  $N_2$ , for example, we assume that the concentration of  $N_2$  quickly reaches an equilibrium solubility  $C_{N_2}^*$  at the surface of the forming TiN layer.  $N_2$  in TiN then diffuses toward the substrate until it encounters other reactants. We postulate the following reactions:



Model equations can now be formulated that are analogous to the equations for argon annealing. For example,  $N_2$  would obey a diffusion-reaction equation similar to (1), with  $C_{N_2} = C_{N_2}^*$  at the exposed surface. TiN would obey a reaction equation analogous to equation (6) for  $TiSi_2$ . Note that the presence of  $N_2$  demands that extra terms be added to equations (1) and (4)-(7).

### Oxygen

Oxygen is commonly observed in experimental analyses of silicides. Typically,  $O_2$  is rejected from forming TiN and  $TiSi_2$  layers and is therefore found between them.  $O_2$  also reacts with some of the species listed above. Although  $O_2$  is technically included in our model, its effect on other species is currently neglected.

### ANALYSIS OF THE MODEL

The above model is quite complex. In general, the equations must be solved numerically to fully capture their content. This has been done in 1D using a standard finite element approximation in which velocities are interpolated quadratically on each element and all other quantities are interpolated linearly between the element endpoints. A fully implicit, mass conserving Euler scheme was used for time integration. An example numerical solution in argon is shown in Fig. 1. Several important properties of the model were observed in the numerical simulations; some of these were also studied with approximate analytic methods. The most important observations for argon annealing are described next.

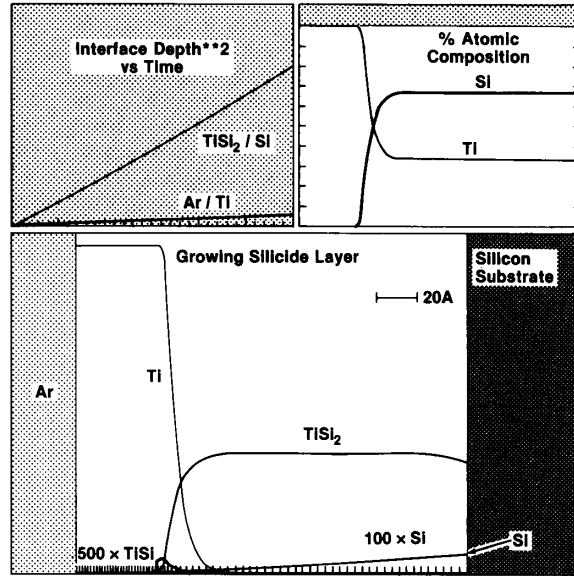


Figure 1. Ti annealed in Ar at 550°C for 60 sec

### $TiSi_2$ /Ti Transition

The equations are capable of modeling arbitrarily abrupt transitions between  $TiSi_2$  and Ti. The evolving layer can be divided into three regions: a surface region that contains mostly unreacted titanium, a substrate region that consists mostly of  $TiSi_2$  and a small amount of diffusing silicon, and an intermediate region of nearly constant width that contains Ti, Si,  $TiSi$ , and  $TiSi_2$ . The intermediate region is approximately delineated by the  $TiSi$  distribution, which has a shape given by the approximate analytic formula

$$C_{TiSi} \approx C_{Ti}^0 / (k_2/k_1 - 1) (e^{-k_1 R x^2} - e^{-k_2 R x^2}), \quad (8)$$

where  $C_{Ti}^0$  is the concentration of the deposited Ti and R is a slowly changing parameter that depends on  $D_{Si}$  and  $C_{Si}^*$ . It can be seen from this that the width of the transition region can be made very small by sufficiently increasing  $k_1$  and  $k_2$ .

### $TiSi$ Detectability

The equations are capable of displaying a  $TiSi$  peak that is detectable only at low temperatures. This is accomplished by adjusting the temperature dependencies of  $k_1$  and  $k_2$  so that  $k_2/k_1$  is small at low temperatures and large at high temperatures. This

behavior can be verified by deriving the peak TiSi concentration from equation (8).

### Parabolic Growth

When  $k_1$  and  $k_2$  are large and  $k_2/k_1$  is also large, the model displays parabolic TiSi<sub>2</sub> growth over nearly the entire growth time. This feature is illustrated in the upper left corner of Fig. 1. The thickness  $x$  of TiSi<sub>2</sub> grown in time  $t$  in this case is approximately given by

$$x^2/t \approx V_{Si} D_{Si}^1 C_{Si}^* \quad (9)$$

Notice that the thickness depends on the product of  $D_{Si}^1$  and  $C_{Si}^*$ . Data published in [1] have been used to estimate  $D_{Si}^1 C_{Si}^*$  for vacuum annealing of Ti films. The result of this is

$$D_{Si}^1 C_{Si}^* \approx 4.1 \times 10^{34} e^{-1.73/kT} / (\text{cm sec}). \quad (10)$$

Unfortunately,  $C_{Si}^*$  is not well known, so  $D_{Si}^1$  cannot be calculated accurately from the above relation. However, it can be shown that the model has a simple scaling property: if  $C_{Si}^*$  is scaled by a factor  $s$  and  $D_{Si}^1$ ,  $k_1$ , and  $k_2$  are scaled by  $1/s$ , then the model solution is the same. Thus, for the purpose of modeling TiSi<sub>2</sub> thicknesses, it is adequate to start with estimated values of  $C_{Si}^*$  and use (9) to infer values of  $D_{Si}^1$ . Figure 2 compares the results from the silicide model with measurements from [1] with  $C_{Si}^*$  equal to about 0.5% of the substrate silicon concentration.

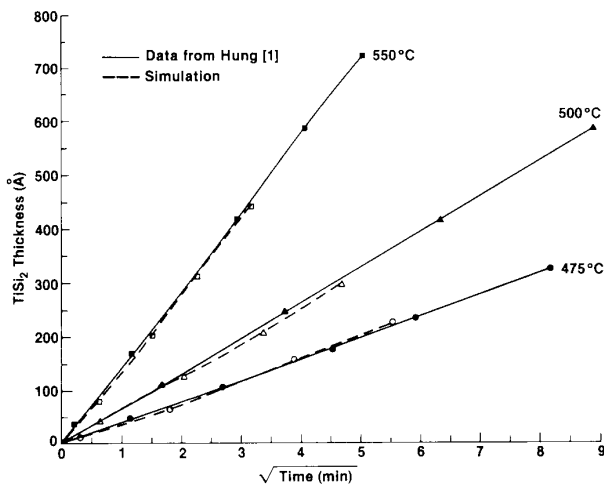


Figure 2. Comparison of simulated TiSi<sub>2</sub> thicknesses with data from [1]

### N<sub>2</sub> Annealing

The silicide model has also been used to simulate nitrogen annealing. Very little is known about the model parameters in this case, but an important qualitative feature of the simulations can be easily understood. After sufficient annealing, the growing TiSi<sub>2</sub> and TiN layers eventually meet. Free nitrogen in the TiN then consumes TiSi<sub>2</sub> releasing silicon. The silicon then diffuses through remaining TiSi<sub>2</sub> and regrows on the substrate, as required by boundary condition (3). This behavior has been observed previously [4] as one of the possible fates for the freed silicon.

### CONCLUSIONS

A model of titanium silicide growth has been formulated that captures many of the reported phenomena. In argon, these include parabolic growth, the appearance of TiSi only at low temperatures, and rapid interface transitions. In nitriding ambients, the model incorporates the growth of competing phases and predicts that silicon released during reactions between nitrogen and silicides will regrow on the substrate.

### REFERENCES

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