

CHARACTERIZATION AND MODELING OF STRESS EVOLUTION DURING NICKEL SILICIDES FORMATION

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ABSTRACT

An curvature measurement technique was used to characterize the stress evolution during reaction of a Ni film and a silicon substrate to form nickel silicide. Stress changes were measured at each stage of the silicide growth. When the nickel films were subjected to long-time isothermal annealing, stresses that developed during silicide formation gradually relaxed. Fitting the experimental results with a kinetic model provides insight into the volumetric strain and relaxation behavior of the reacting film and the reaction product.

1. INTRODUCTION

The stresses observed during silicide formation show an overall trend of compressive stress [1]. All formation of refractory metal silicides causes compressive intrinsic stress. For transition metal silicides, some literatures [2-4] show that the formation of Pd₂Si, Pt₂Si, Co₂Si and CoSi₂ causes compressive stress, while there are some contradicting reports [5-6] showing that the formation of Ni₂Si, Co₂Si and Pt₂Si causes tensile stress. The reason for this inconsistency is not fully understood though it is commonly attributed to the different experimental conditions. Thus, more experiments are needed for each material system to confirm the type of stress generated by the reactions. The experimental system used in this study is the binary Ni and Si system. Koos et. al. [5] conducted the earliest experiment on the silicides of evaporated nickel films. Tensile stress was observed by Koos et. al. during the formation of Ni₂Si. This was opposite to the compressive stress observed by Tsai et. al. [9] during the formation of Ni₂Si.

A model for the stress evolution during the formation of silicides was also developed. Zhang and d'Heurle [7] proposed a model that took into account the simultaneous stress formation due to the reaction and the relaxation of stresses. The model also included an important parameter, which was the stress induced by the reaction at

the instant of reaction, which would help in understanding the origin of stress generated during the reaction. The model provided a satisfying qualitative picture of stress evolution during the formation of Pd₂Si and TiSi₂. No work was done to compare the stress changes during nickel silicides formation and the model before. Buad et. al. [8] tested his experimental data for Pd/Si system with the model. However, the intrinsic stress at the instant of silicide formation was not reported in his paper.

In the present work, stress development and relaxation during the formation nickel silicides was studied using the curvature measurement technique. The experimental data was fitted with the Zhang and d'Heurle's model.

2. EXPERIMENTS

The nickel film was deposited on HF cleaned Si (100) substrate using magnetron sputtering at the vacuum level of 5x10⁻⁷ torr. Sputtered sample was then annealed in-situ in FSM thin film stress gauge in which curvature changes during reaction was measured. The annealing ambient was forming gas consisting of 96% N₂ and 4% H₂. The force per unit width (F/W) in the film could be calculated from the measured curvature changes using the Stoney equation [10]:

$$\frac{F}{W} = \sigma_f t_f = \frac{E}{6(1-\nu_s)} t_s^2 (K - K_o)$$

where σ_f is the stress in the film, t_f is the film thickness, F is the force in the film, W is the width of the sample, E_s is the Young's modulus of the substrate, ν_s is the poisson ratio of the substrate, t_s is the substrate thickness, K is the measured curvature, and K_o is the initial curvature.

The first experiment involved annealing the sample at a constant heating rate of 5°C/min from room temperature to 600°C. In the second

experiment, the sample was annealed isothermally at temperature ranging from 230°C to 250°C for 4 hours. After the stress measurement, the samples were analyzed using XRD, SEM and TEM to identify phases and structural changes in the film.

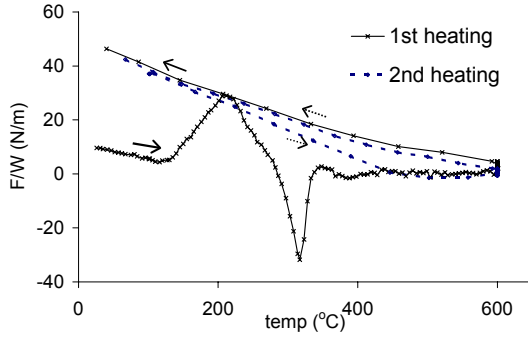


Figure 1 Plot of the total force per unit width verse temperature for 30 nm Ni/Si annealed at 5°C/min to 600°C

3. RESULTS AND DISCUSSIONS

(A) Characterization of total force per unit width changes during silicidation process

Fig. 1 shows the changes in F/W in nickel film on Si as a function of temperature during the heating cycle with a constant ramping rate. The curve for the first heating cycle shows a maxima at 210°C and two minimas at 317°C and 388°C respectively. The results agree with the result Tsai et. al. reported [9]. The two minimas were proven to be related to the formation of Ni₂Si and NiSi at 317°C and 388°C respectively.

Tsai et. al. [9] also reported that no nickel silicide was formed after the film was heated to 234°C. Thus the first maxima can only be attributed to morphological changes in nickel film. From the literature, Knauth et. al. [11] reported that nickel film experienced grain growth after being annealed at the temperature range between 150-300°C. In the present work, four point probe measurement showed a drop in sheet resistance of the film from 11.6 to 9 mohmcm after being annealed from room temperature to 200°C. It is known that the grain growth in thin film will give a drop in the sheet resistance of the film [12]. Therefore, the initial increment of tensile stress should be due to grain growth in nickel film.

During the second heating cycle, the forces in the film changed linearly with increasing temperature. The features observed in the curve for first heating cycle were absent, indicating that the film had fully transformed into NiSi, as shown by Tsai et. al.

To understand the origin of the force changes in the film, we need to look at the volume changes caused by the reaction, which the literature [1] had extensively discussed. In Table 1, the volume changes during the formation of Ni₂Si are listed. Two sets of numbers are presented in this table. The first of these is the fraction of the final volume to the initial volume of the reactants (nickel plus silicon), which shows a considerable reduction. The second number shows the relative volume expansion undergone by silicon upon alloying with nickel to form Ni₂Si. This volume change is quite huge and can be used to explain the compressive stress caused by Ni₂Si formation.

The analysis for the formation of NiSi is more complicated as two reaction interfaces are involved. Firstly, one Ni is released from Ni₂Si, which causes 35% volume decrease in the Ni₂Si layer. Following that, the released Ni atom would diffuse into Si to form NiSi, which causes 11% volume increment at the NiSi/Si interface. The net result of these two steps would lead to an increase in free volume in the Ni₂Si and in turn should generate a tensile stress. However, this is in contradiction with what is shown in Fig. 1. This result shows that the current understanding on the volumetric changes that causes stresses at reaction interface is not sufficient in explaining reaction that involves multi-interface. Relaxation process at different interface may need to be taken into account.

Table 1 Volume changes during the formation of Ni₂Si

Molar volume of reactants		Volume fraction of reaction product to reactants	
Ni	Si	Ni ₂ Si/(Ni+Si)	Ni ₂ Si/(Si)
13.18	12	0.78	1.62

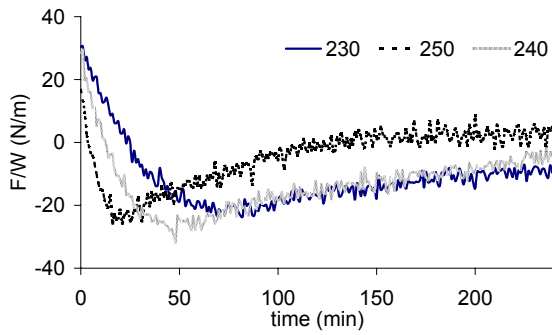


Figure 2 Plot of total force per unit width versus time for 30 nm Ni/Si annealed at 230-250°C for 240 min

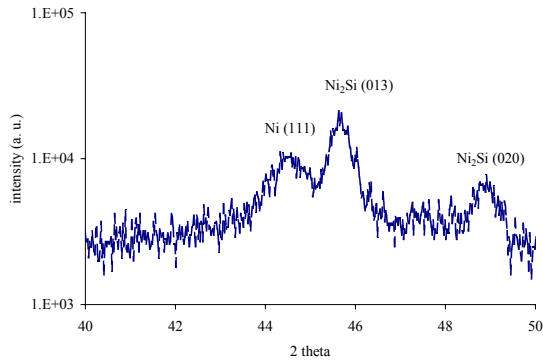


Figure 3 XRD spectrum of nickel film annealed at 250°C for 240 min

Fig. 2 shows the force changes during the formation of Ni_2Si while 30 nm sputtered nickel film on Si (100) substrate was heated isothermally at 230°C, 240°C and 250°C. Compressive stress in the film increased at the beginning of the isothermal hold. After 20-50 minutes of annealing, the value of the compressive stress relaxed.

Fig. 3 shows the XRD spectrum for the film after annealing for 240 minutes at 230°C. The spectrum showed that nickel and Ni_2Si were the only two phases in the film after the annealing. The morphology of the film after the annealing was investigated using SEM and TEM. Fig. 4 shows SEM micrograph of the sample annealed at 230°C. Discontinuities appeared on the films after extensive annealing. The cross section of the sample observed using TEM (as shown in

Fig. 5) showed that two phases coexisted after the nickel film was annealed at 230°C for 240 minutes. The upper layer was un-reacted nickel while the bottom layer was Ni_2Si . The un-reacted nickel film became discontinuous after being annealed for 240 minutes. The discontinuities could be a result of agglomeration of the un-reacted nickel film. The nickel film could agglomerate, as it became thinner while reaction proceeded. As the nickel film became discontinuous, the stress in the nickel film could be negligible. The forces change observed in Fig. 1 could be predominated by the forces induced by the formation of Ni_2Si .

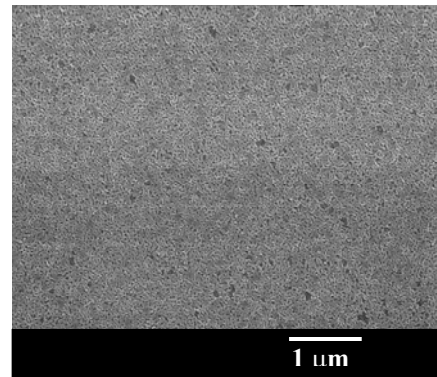


Figure 4 SEM image for 30 nm nickel film annealed at 230°C for 240 min

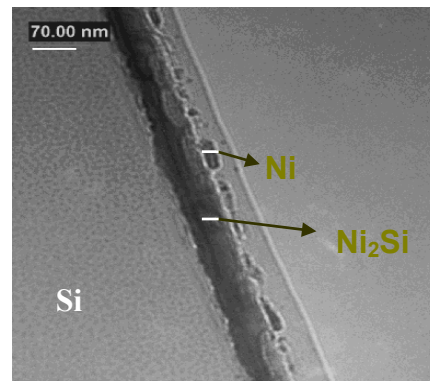


Figure 5 TEM micrograph for nickel film annealed at 230°C for 240 min

(B) Modeling the stress evolution during the reaction

Result shown in Fig. 2 was fitted with Zhang and d'Heurle's model. Major assumptions in the model are as follow:

- (1) stress builds up through layer silicide growth,
- (2) stress relaxes in growing silicide layer through Coble creep

In this model, two forces are considered. They are forces due to compound formation, F_s and forces in the un-reacted film film, F_m . The total forces measured during silicidation, F is the sum of these two. These two forces are briefly explained as follow:

(i) Forces due to compound formation, F_s :

The silicide is divided into n sublayers of thickness Δl , each with an instantaneous stress σ_{is} . σ_{is} is equal to the intrinsic stress induced by the reaction, σ_{in} subtracted by the relaxed stress, σ_{rel} . The overall force in the growing layer, F_s at any time t is the sum of forces over all layers, as given by the following expression. By assuming coble creep, and diffusion controlled growth, F_s is given by the following expression:

$$F_s(t) = \left[\sigma_{in} \int_0^{l(t)} \exp\left(\frac{l'^2}{k\tau}\right) dl' \right] \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where k is the parabolic constant and τ is the relaxation time for the silicide.

(ii) Forces in the un-reacted film, F_m :

As the reaction proceeds, forces in the remaining un-reacted film will decrease not only as a function of its specific relaxation but also the decreasing film thickness. At zero time, when the reaction just begins, the metal film is under a uniform stress, σ_m . The force in the film will be equal to $\sigma_m \beta l_0$. Here β is the ratio of the metal thickness to the corresponding silicide thickness, βl_0 is the initial thickness of the metal film. At the temperature of reaction the stress in the metal film relaxes with a relaxation time τ_m . The force in the film decreases as a function of the film consumption rate as well. Combining these two effects, F_m is given by

$$F_m = \sigma_m \exp\left(-\frac{t}{\tau_m}\right) \beta \left[l_0 - (kt)^{1/2}\right] \quad (2)$$

Finally, the total force developed during the silicidation process is given by this expression:

$$F = F_s + F_m \quad (3)$$

Figure 6 shows the fitting curves for nickel film annealed at 250°C. It illustrates how the force in the unreacted metal films, F_m and the force in the silicide F_s evolve during the annealing cycle.

Data obtained from the fitting of the experimental result with the model is shown in Table 2. Relaxation time, τ of Ni_2Si is found to follow the Arrhenius behaviour. Activation energy calculated from this data is 1.81 ± 0.29 eV (shown in Figure 7). This is close to the activation energy for Ni diffusion through Ni_2Si (1.71eV) [13]. Hence Ni diffusion could be the limiting phenomenon controlling the relaxation of this compound. This verifies the assumption of Coble creep in this model.

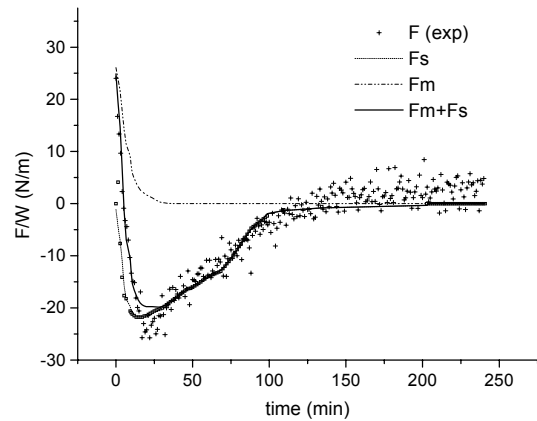


Figure 6 Force changes (experimental and theoretical) in nickel film (30 nm) annealed at 250°C for 240 min.

Table 2 Curve fitting result for 30 nm nickel film annealed at different temperatures

Temperature (°C)	σ_{in} (GPa)	τ (min)
230	-2.86	79
240	-1.5	28
250	-1.65	16

From Table 2, we also find the compressive stress caused by the reaction, σ_{in} to be 2.1 ± 0.54 GPa. The stress changes in the plane of the film is related to the volumetric strain in the film by this equation:

$$\Delta\sigma = -\frac{E}{(1-\gamma)} \frac{\Delta}{3}$$

where Δ is the volumetric strain, $E/(1-\gamma)$ is the biaxial modulus of Ni_2Si . Taking E of Ni_2Si from the literature as 161 GPa and assuming that γ is 0.33, when the stress is 2.1 GPa, the volumetric strain is 1.29%. This value is much smaller than 62% as shown in Table 1. Such a large difference shows that the current way of estimating the volumetric strain caused by reaction is not correct, or it is also possible that there is a huge stress generated before it can be measured by the current experimental method.

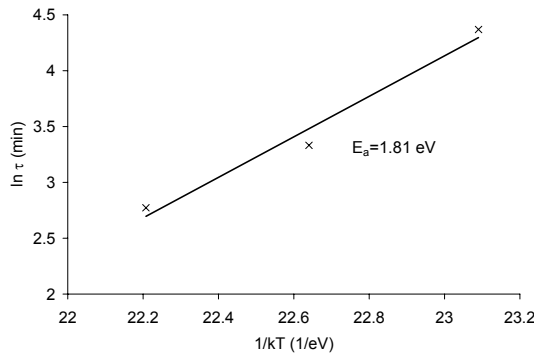


Figure 7 Arrhenius plot of relaxation time, τ of Ni_2Si

4. CONCLUSIONS

Formation of Ni_2Si causes a compressive intrinsic stress. This agrees with the expectation of a volumetric expansion at the Ni_2Si/Si interface. Forces caused by the formation of $NiSi$ are difficult to understand due to the presence of two reaction interfaces. The force changes during the formation of Ni_2Si were well fit using a model proposed by Zhang and d'Heurle. The relaxation data obtained from the fitting data

indicates an activation energy close to the activation for the diffusion of nickel through Ni_2Si . Thus, Coble creep is a plausible mechanism controlling the relaxation of stresses developed during the formation of Ni_2Si . The volumetric strain caused by the reaction calculated from the fitting result is very low compared to the molar volume change during the reaction. The reason for this is not yet understood.

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