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In-situ investigation by X-ray diffraction and wafer curvature of phase formation and stress evolution during metal thin film – silicon reactions

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Abstract. Metal silicides are important materials for microelectronic devices. They are formed via a solid state reaction between a metal film and a silicon substrate. Mechanical stresses arise during this reactive diffusion process and are investigated by x-ray diffraction and curvature measurements. The different phases that form, yield distinct stress evolutions related to the volume change and to the mechanical properties of the silicides. In the formed silicide layers strains can vary strongly from one grain to the other as shown in NiSi, where it is attributed to the strong anisotropy in thermal expansion.

Introduction

The invention of planar technology in 1959 by R. Noyce and J. Kilby [1] has launched a steady and impressive rate of miniaturisation in the size of integrated circuits. The figure-of-merit, which is often used to characterize a technology node, is the channel length of an elementary transistor. At the time of this writing, i.e. the end of year 2006, we are at the cross point between generation 65 nm and generation 45 nm. Such a trend towards smaller and smaller devices has been made possible through the introduction of new materials: low-k dielectrics for interconnects, high-k dielectrics for gate oxides, etc. Si-based microelectronics has been and still is a fantastic playground for materials scientists. Transition metal silicides are an important example of such an innovative use of advanced materials to fulfil new functions in advanced integrated circuits. They have been introduced in silicon devices at the beginning of the eighties and are used to decrease access resistance at the source and drain as well as a shunt to the high gate polysilicon resistance. Indeed a rather large number of metal silicides are good electrical conductors with room temperature resistivities ranging between 10 and 20 μΩcm [2]. The first silicides, which have been used as gate contacts, were refractory metal silicides such as WSi_2. Such a choice was driven by the need for a good thermal stability at elevated temperatures. The decreasing thermal budgets in small dimension devices have triggered changes towards new silicides: $TiSi_2$ and then $CoSi_2$ because the transition temperature from the high resistivity C49 $TiSi_2$ (space group C_{mcm}) to the low resistivity C54 $TiSi_2$ (space group P_{ddd}) was becoming too high in narrow features. Ever shrinking dimensions are nowadays imposing a new change because, among others, Si consumption during $CoSi_2$ formation by reactive diffusion is too large to be compatible with shallow junction formation. NiSi has been chosen because of its low resistivity, low formation temperature and low Si consumption [3]. It has, however, an important drawback: for the first time one is using a silicide, which is not the silicon-richest one. Because $NiSi_2$ formation is nucleation-controlled [4] there is indeed a temperature window within which NiSi does not react with silicon to form $NiSi_2$. The risk of unwanted $NiSi_2$ formation in localized areas does, however, exist. It has been proposed [5] to add Pt to the initial Ni layer in order to improve NiSi stability with respect to silicon.

Silicide layers are generally formed via a solid state reaction between a thin metal film and poly- or single crystal silicon. The sequence and kinetics of phase formation raise a number of very fundamental questions [6,7] and are still an area of intense research [3]. It is now well established [6] that when the driving force for silicide formation is small enough reaction kinetics are controlled by nucleation. This results generally in a rough surface morphology. When the nucleation step is not rate-controlling a diffusion-controlled reaction is observed with a sequential [8] formation of phases. Metallization of Si_xGe_{1-x} alloys, which have appeared in Si technology in 1986-1987, raise very similar issues [9] and a number of studies are being published nowadays on the formation of nickel silico-germanides.

The formation of a silicide film by reactive diffusion yields very high mechanical stresses [10,11] because of the high volume change involved. These stresses have, however, been comparatively less studied than the formation kinetics although this is increasingly considered an important issue. Indeed strain engineering of the electrical properties of silicon devices is now currently being considered [12] as a way to improve performances. Stresses that develop as a result of interdiffusion or of the appearance of a new phase is a very general problem in metallurgy. For example the development of stresses during the oxidation of metals [13] has long been recognized as a key factor, which determines the adhesion of the oxide scale. Quantitative modelling has proved, however, extremely difficult. This is partly related to the strong coupling between kinetics, thermodynamics and mechanics [14-16] which has to be taken into account to describe such a problem.

This manuscript is focused on recent experiments on the Ni-Si system. Coupled curvature and X-ray diffraction measurements are presented first. In a second part a few basic ideas for a qualitative understanding of stress development are given. The last part is devoted to the strains in the polycrystalline NiSi films.

Stress development during the formation of nickel silicides

Combined synchrotron x-ray diffraction and wafer curvature measurements during Ni-Si reactive film formation

The top of figure 1 shows the evolution of the force applied on the Si (001) substrate while reacting a 13 nm Ni film with Si at 2°C/min. Such measurements are performed by monitoring the substrate's curvature and applying Stoney's formula [17], which links curvature to the force F per unit width applied by the coating on the substrate. There is clearly a very complex stress evolution, whose understanding calls for additional structural measurements. We have developed a specific experimental set up [18] where synchrotron x-ray diffraction is performed at the same time as the substrate curvature is monitored. Such an experiment yields invaluable information on the stresses that develop during growth as well as the phases that appear. Coupled curvature and x-ray diffraction measurements [18] were performed at LURE H10 beam line with an incident wavelength of 0.16314 nm. During heating at a constant heating rate of 2°C/min the angle of incidence of the x-ray beam on the sample was fixed at 24°, which corresponds roughly to the Bragg angle for the expected diffraction lines (Ni 111, Ni_2Si 301/121, Ni_3Si_2 350 or NiSi 112). The diffracted rays were recorded using a curved position sensitive detector spanning 120° with a 30 s counting time. Wafer curvature measurements were performed every 30 s via a home-made laser scanning technique. In order to increase wafer curvature, the Si substrate had been thinned down to 130 µm prior to in situ annealing. Thanks to the coupled curvature-X-ray diffraction experiment shown in figure 1 a detailed understanding of the different stages of stress development can be obtained. The tensile stress buildup below 115°C is caused by Ni grain growth. Above 115°C the compressive evolution is caused by Ni_2Si growth. Ni_3Si_2 starts to grow at 170°C and causes the increasing compressive slope. The deep minimum at 210°C corresponds to the complete consumption of Ni. NiSi starts forming at 230°C, which corresponds to the second tensile maximum. NiSi forms initially at the expense of Ni_3Si_2, which has completely disappeared at 240°C, i.e. at the second shallower compressive minimum. Beyond 240°C NiSi keeps growing at the expense of Ni_2Si.

Stress development during Ni-Si reaction is indeed a very complex situation where three different phases may coexist. Taking into account the amount of uncertainty that still remains to describe properly stress evolution during the growth of a single silicide, one should stay modest and limit oneself to a qualitative description. Simple volume change arguments may explain the most important variations [19] observed in Fig. 1, although one should remain cautious when several interface reactions have to be taken into account. Two important remarks can be done on this force evolution: 1) The transient formation (170 – 240°C) of Ni_3Si_2 seems to play a major role in the stress evolution. 2) The higher the temperature the smaller the stress variations. This observation seems to apply to other metal-silicon systems (Co-Si for example [20]). There are at least two reasons that may explain this behavior. The first one is that stress relaxation is more rapid at higher temperatures. The second one is that volume changes tend to be smaller, at least compared to the initial volume change between pure silicon or metal and the first silicide to be formed.

Modelling

Figure 2.a shows typical measurements of force per unit width deduced from substrate curvature measurements during the growth of Ni_2Si from the reaction of a Ni film with Si (001). Here the silicide that forms is the first one in the phase sequence. The force evolves towards compression reaches a compressive maximum and relaxes progressively towards zero. This indicates that if one waits long enough, the formed silicide is stress free at

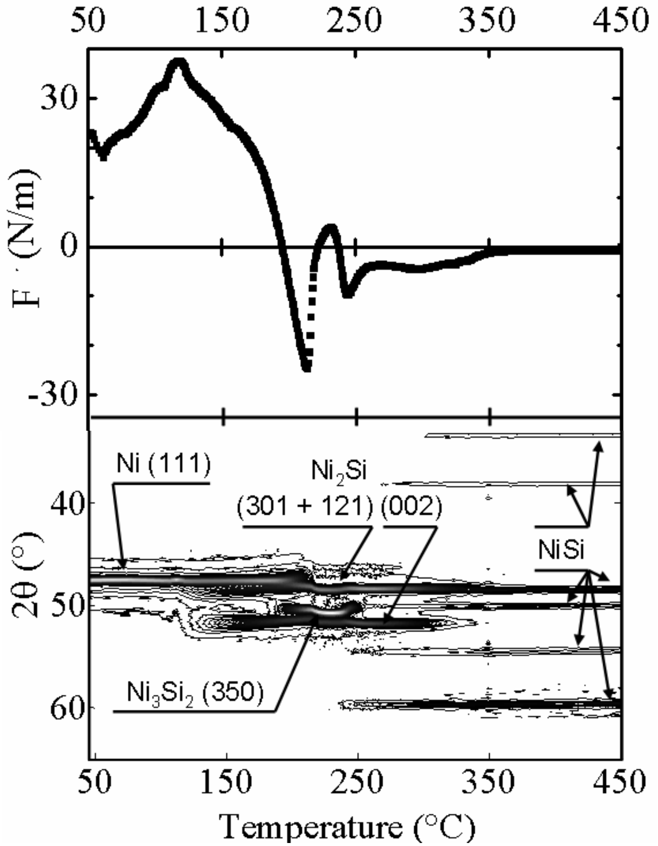


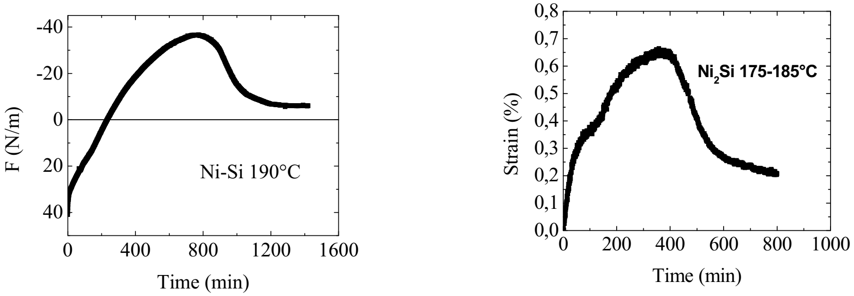
Figure 1. In-situ combined wafer curvature measurement and X-ray diffraction measurement during reaction of a 13 nm Ni film with a Si(001) substrate. Heating rate is 2°C/min.

the growth temperature and the room temperature stress after cooling does not contain any information about the growth stress. On the other hand the stress vs cooling temperature contains interesting information about the stress relaxation process in the silicide.

The formation of a new phase from the initial reactants implies a considerable change in volume. This is thought to be the origin of the stress that develops during growth. For stresses caused by metal oxidation, it is customary to refer to the Pillings-Bedworth relation between the volume of metal and the corresponding volume of oxide. In a thin film, which is attached to a rigid substrate, the volume change has to be accommodated by in-plane strain which implies compressive stress buildup in the silicide layer. This is because the reaction takes place at a specific interface. Let us consider the growth of Ni_2Si from the reaction of Ni with Si. Since Ni has been shown [21] to be the most mobile diffusing species in Ni_2Si, the reaction occurs at the Ni_2Si/Si interface. Thus the volume change is

$$\frac{\Delta V}{V} = \frac{V_{Ni_2Si} - V_{Si}}{V_{Si}} \qquad (1)$$

which is positive. One expects therefore a compressive stress to develop in agreement with experimental observations.



(a) (b)

Figure 2. a) Curvature measurements during Ni 18 nm thin films reacting with silicon (001) at 190°C. b) Ni_2Si 020 x-ray diffraction peak position vs time at 175-185°C.

From a quantitative point of view, things appear far less clear. The volume change which appears in equation (1) is enormous: in the case of Ni_2Si growth, it is 66%, which would yield a biaxial stress enormously higher than the theoretical critical shear strength. Sucn an isotropic volume expansion is not realistic and a classical solution for this problem is to consider an anisotropic volume change [22]. Experimentally, the initial stress in the silicide is of the order of -2 GPa.

Stress relaxation is the second key ingredient to describe the way stress develops in the growing silicide film. Once growth is completed, as shown in Fig. 2.a, stress relaxation dominates. During the growth one expects stress buildup and relaxation to occur simultaneously. The stress relaxation mechanism at work is a complex problem for at least two reasons: 1) it depends necessarily on the microstructure which is bound to change as growth proceeds, 2) stress relaxation mechanisms in thin films are known to differ significantly from their bulk counterparts. In particular the film thickness [23] controls directly the yield strain in metal layers. A striking example of how silicide microstructure may influence stress relaxation and thus stress buildup has been shown in Pd_2Si [24] grown either on Si (001) or on Si (111). It is clearly seen that stress relaxation is much faster on Si (100) than on Si (111), which yields to a higher maximum force on Si (111). The different behaviors result directly from the different microstructures of the two films. Indeed hexagonal Pd_2Si grows epitaxially on Si (111) while Pd_2Si on Si (001) is polycrystalline with a (00.1) fiber texture. The very large difference in relaxation rate between the two silicide films may be explained through plasticity arguments. In an hexagonal structure such as Pd_2Si it is likely that dislocation glide occurs in (00.1) basal planes. There is, however, no resolved shear stress on these planes when they are parallel to the film surface. But grains whose orientation is significantly off the surface normal (the mosaic spread is 20° on Si (100)) will experience a non zero shear stress and may thus be caused to yield.

Zhang and d'Heurle [25] have proposed a phenomenological model which accounts reasonably well for the observed F(t) behavior. The model describes the evolution of the force as a result of competing stress build-up due to volume change and stress relaxation. The force arising from the former occurs at a rate given by the growth rate, while the latter depends on the stress relaxation mechanism at work. In the original paper a Newtonian viscous flow relaxation was assumed with a relaxation time τ. In short, the stress at location z (measured from the growing interface) within the silicide film is the instantaneous growth stress σ_0, which has relaxed by an amount related to the time when this particular slice dz was formed

$$\sigma(z,t) = \sigma_0 \exp\left(-\frac{t - h^{-1}(z)}{\tau} \right) \tag{2}$$

where z=h(t) is the growth law. For a diffusion controlled growth one gets

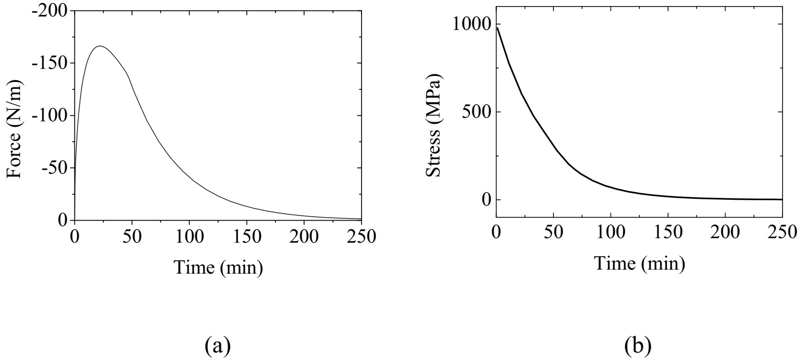
$$h(t) = \sqrt{Dt} \text{ or } h^{-1}(z) = \frac{z^2}{D}. \tag{3}$$

The force F(t) is then obtained by integrating $\sigma(z,t)$ from z=0 to z=h(t). This simple model depends on three parameters, two of which can be extracted in a straightforward way. Indeed the rate D can be determined independently and τ can be extracted from F(t), which is proportional to $\exp(-t/\tau)$ once the silicide growth is completed. A calculated F(t) is shown in figure 3.a. The comparison with experimental data shows that the model accounts reasonably well for the observed behaviour. This agreement is, however, lost when one considers the average stress in the silicide, which can easily be calculated from

$$\sigma_{av}(t) = \frac{1}{h(t)} \int_0^{h(t)} \sigma(z,t)\,dz \tag{4}$$

and is shown in Fig. 3.b (using the same parameters as for Fig. 3.a). The calculated average stress decreases continuously from σ_0 on. The average stress in the growing silicide layer can be monitored experimentally through the position [26] of x-ray diffraction peaks. Fig. 2.b shows the evolution of Ni_2Si 020 peak position during annealing at 185°C (in fact the experiment was started at 175°C and the temperature was increased to 185°C after 150 minutes, which explains the break in the curve). The nice agreement which appeared for F(t) between experiment and modelling is no more there. This strong disagreement between model and experiment remains unsettled.

The time-dependent stress from equation (2) does not apply to a ramp experiment as shown for example in figure 1. Indeed the relaxation time is temperature-dependent. The resolution of the full time and temperature dependence has been performed in [22].



(a) (b)

Figure 3. Force (a) and average stress in the silicide layer (b) according to Zhang-d'Heurle model

Stresses in the formed NiSi layer

Going back to figure 1 the only remaining phase at 350 °C is NiSi. It is polycrystalline as seen from the different Bragg peaks that appear in the diffraction spectrum. NiSi is orthorhombic (MnP structure a = 0.5233 nm, b = 0.3258 nm, and c = 0.5659 nm) and exhibits an amazingly large anisotropy in thermal expansion coefficients: $\alpha_a = 42$, $\alpha_b = -43$ and $\alpha_c = 34$ 10^{-6} K^{-1} [27]. One thus expects extremely large grain-to-grain strain variations ($\Delta\alpha\Delta T$) in polycrystalline films. Figure 4 shows strains normal to the film surface in (103) and (112) oriented grains [28]. As expected there is a considerable difference in strain between these different grains. The unstrained lattice spacing, which is needed for strain calculation, has been calculated from [27]. The linear and reversible variation of (103) lattice spacing with temperature indicates a thermoelastic behavior. This in agreement with the study by the IBM group [29], where is has been shown that stress relaxation does not occur below 500 °C.
This behavior clearly points to the strong temperature dependence of the yield stress in metal silicides. Although the mechanical properties of NiSi are still unknown, one may look into the few studies which have been performed on bulk transition metal silicides. A strong dependence of critical resolved shear stresses on temperature is always found, which is indicative of deep Peierls valleys.

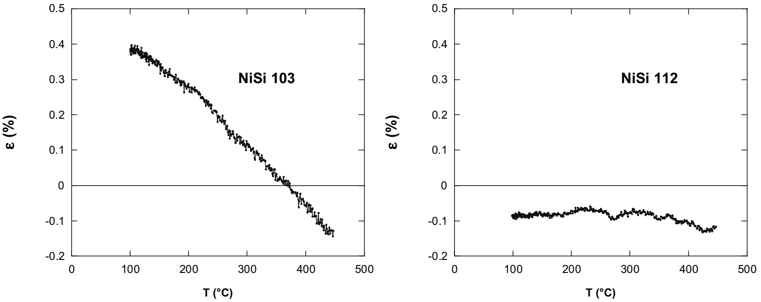


Figure 4. Normal strains in NiSi as a function of temperature. A large difference is observed between different grain orientations.

Concluding remarks

This short review was dedicated to the mechanical stresses that develop during reactive diffusion between a metal thin film and a silicon substrate with a particular emphasis on the Ni-Si system. Combined synchrotron x-ray diffraction and wafer curvature measurements have proved extremely useful in investigating the stresses that appear as a result of intermetallic formation. X-ray diffraction allows also the measurement of strains in the different phases that form as well as in the different crystal orientations that are present in the polycrystalline layers. The complexity of the processes (coexistence of several phases, low symmetry crystal structures, unknown mechanical properties, etc) prevent so far a complete modelling but a reasonably good understanding may be obtained from phenomenological models. Very fundamental issues such as the proper description of the stress evolution in the silicide film remain, however, unsettled. Future work should also focus on local strains, which seem to be highly inhomogeneous.

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