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Investigation of the silicon beading phenomena during zone-melting recrystallization

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During recrystallization of encapsulated silicon films on SiO_2 , by the graphite strip heater technique, the silicon sometimes breaks apart and agglomerates into small beads or stripes. By secondary ion mass spectroscopy analysis, it was found that a high concentration of nitrogen at the interface between the silicon and the top SiO_2 capping layer is needed to prevent this from occurring. Incorporation of hydrogen into the crystallization ambient was found to cause the beading to occur. The initial stages of the bead formation were investigated by scanning electron cross-section microscopy.

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During the recrystallization of encapsulated silicon films on SiO₂, by the zone melting technique of Geis *et al.*,¹ the silicon film sometimes breaks and tends to agglomerate into small beads or stripes. The visual appearance of this effect is such that the silicon film seems to be stripped off from large portions of the surface area and therefore we shall refer to this phenomenon *as stripping*.

To avoid the stripping, Maby *et al.*² have found it necessary to sputter a thin Si_3N_4 film on top of the chemical vapor deposited (CVD) SiO_2 encapsulation layer. On the other hand, Lam *et al.*³ have found that capping by a plasma CVD SiO_2 alone yielded their best results. The stripping phenomenon and its causes have not been well understood although it was suggested that the presence of nitrogen in the encapsulation layers improves the wetting properties of the molten silicon.^{1–3} In this letter it is shown that interfacial nitrogen is necessary to prevent the stripping and that hydrogen can cause it to occur. Also, the initial stages of bead formation have been investigated by scanning electron microscope (SEM) cross-section microscopy.

Our recrystallization experiments were done in a graphite strip heater oven in a manner similar to that of the Lincoln Laboratory group.¹ The wafer was supported on a graphite heater by means of small quartz spacers of 0.5-mm thickness. The wafer was first heated to about 1200 °C and then moved under the top stationary graphite strip at a speed of 2 mm/s. The top graphite strip was heated to about 1700 °C. Experiments were usually performed in an N₂ ambient and tests were also done in Ar, He, or a mixture of H₂(10%)/Ar(90%) ambients.

The cross section of the samples is shown in the inset of Fig. 1. The bottom SiO₂ layer was thermally grown to a thickness of 0.5 or 1 μ m. The polysilicon film was deposited by low pressure CVD from SiH₄ at 620 °C and its thickness was 0.25 or 0.5 μ m. The top SiO₂ layer was deposited by atmospheric pressure CVD from SiH₄, N₂O, and N₂ at 820 °C and its thickness was 0.5, 1, or 2 μ m. Finally the thin (30 nm) Si₃N₄ was deposited by low pressure CVD from SiH₂Cl₂ and NH₃ at 820 °C.

Depth profiles of ¹⁴N were obtained from a CAMECA IMS-3F secondary ion mass spectrometer (SIMS). High

mass resolution was required to discriminate against the presence of the ²⁸Si⁺² ion which has an equivalent mass of 14. Nitrogen in the top 30-nm-thick Si₃N₄ layer is evident in the large initial peaks seen in both curves (b) of Figs. 1 and 2. The broadly varying nitrogen level within the oxide film is due mainly to surface charging effects as was determined from separate profiles of ²⁸Si which showed similar level variations. The nitrogen levels within the oxide and at the interfacial peaks in Fig. 1 were not calibrated due to the lack of suitable standards.

SIMS profiles of ¹⁴N for samples exhibiting smooth crystallization are shown in Fig. 1 and profiles for samples exhibiting stripping are shown in Fig. 2. The appearance of a N



FIG. I. Secondary ion mass spectroscopy (SIMS) profiles of ¹⁴N for samples which crystallize smoothly. The nominal thicknesses of the films were $Si_3N_4:29 \text{ nm}$, CVD top $SiO_2:902 \text{ nm}$, Si: 260 nm, bottom thermal $SiO_2:500 \text{ nm}$. Curve (a) is for a sample whose nitride was etched off and was measured prior to crystallization in the oven. Curve (b) was measured after crystallization on a sample which had both the nitride and about a third of the top oxide etched off.



FIG. 2. SIMS profiles of ¹⁴N for samples which exhibited stripping and silicon beading. Curve (a) is for a sample which did not have a nitride layer and curve (b) for a sample with the nitride layer as shown in the inset of Fig. 1. Both curves were measured on regions adjacent to the stripped area, after the samples had been processed in the oven. Notice the absence of the interfacial peak which is seen in Fig. 1 at the Si- (top) SiO₂ interface.

peak at the top SiO_2 -Si interface (Fig. 1) was found to correlate well with the absence of stripping on these and other samples as well.

Curve (a) in Fig. 1 was obtained from a sample which had its top nitride film etched off, in hot phosphoric acid and which did not undergo the recrystallization process. The data show that the N peak already exists at the interface prior to crystallization. Curve (b) was taken on a sample after it had been crystallized, and which had all layers in place. Curve (c) was taken on a sample which was crystallized *after both the nitride and about a third of the oxide* had been etched off. These etching experiments show that the oxide thickness and the presence of a top nitride during the crystallization process are not critical for obtaining smooth results. It is seen that the determining factor is the existence of the interfacial nitrogen.

The data shown in Fig. 2 were taken on samples which had been processed in the oven, on regions adjacent to the stripped area. Curve (a) is for a wafer that had no nitride and curve (b) is for a wafer that had the nitride film but still exhibited stripping. It is seen that the absence of the interfacial N peak correlates with the appearance of stripping.

It was already found by Maby *et al.*² that CVD nitride does not yield reproducible results and this was our experience as well. A CVD process was chosen because it is a standard process in silicon technology. We have also experimented with sputtered nitride and found that it too produced variable results depending on the existence of the interfacial nitrogen. The exact composition of this interfacial region and the mechanism by which it grows still remain to be identified.

To provide more understanding of the stripping phenomena, the morpohology of the surface after crystallization



FIG. 3. Optical photomicrographs of samples processed in the oven. (a) shows smooth crystallization for a sample whose SIMS profile is similar to Fig. 1. (b) shows the silicon beads in a sample whose SIMS profile is similar to Fig. 2. (c) shows a sample processed in $H_2(10\%)/Ar(90\%)$. (d) shows a wavy oxide film surrounding a long silicon stripe.

is shown in the series of optical photomicrographs of Fig. 3. Photograph (a) shows smooth crystallization occurring in a sample whose SIMS nitrogen profile is similar to that of Fig 1. Silicon beads formed in a sample whose SIMS data are similar to Fig. 2 are shown in photographs (b). In the lower (b)photograph the transition from the nonmelted rough silicon film to the stripped beaded area is seen. The smooth surface around the silicon beads belongs to the top oxide layer which sometimes remains sticking to the bottom oxide. In the upper (b) photograph a region where the top oxide film lifts or pops up is indicated by an arrow. This popping up was seen sometimes to occur and continue propagating during the optical microscope observation. It is well known that an oxide film on silicon is under compressive stress and when it is released it becomes wavy. Such a wavy appearance is shown in Fig. 3(d) where the silicon has agglomerated into a long stripe rather than a bead.

While the sample shown in Fig. 3(b) is an example of results obtained in a N_2 or an Ar ambient, the sample shown in (c) was done in a hydrogen-containing ambient (10% $H_2/$ 90% Ar). It is seen that the beads are smaller and more numerous, presumably because more holes form in the silicon film during the initial stage of the stripping, which is described below.

The initial stages of the stripping and bead formation are shown in Fig. 4 The SEM micrographs were obtained

FIG. 4. SEM cross-section micrographs obtained from a sample in which the stripping was frozen by a sudden jet of He gas. (a) shows the initial stage of bead formation: notice the gradual increase in the silicon film thickness. (b) is a magnified view of the left edge of micrograph (a). Holes formed in the silicon film in other locations are shown in (c) and (d).

from a cross section of a sample where the stripping was frozen by impinging a He flow on the sample in a manner similar to Geis *et al.*¹

Micrograph (a) shows the beginning of bead formation. Notice the gradual increase in the silicon film thickness towards the center of the micrograph. The top oxide film smoothly covers the silicon and is broken on the left side where it hangs over the curved edge of the silicon film. A magnified view of this corner is shown in (b). The contact angles between the frozen silicon and either the top or bottom oxide layers are about $110^{\circ}-120^{\circ}$. Such a contact angle indicates poor wetting between the films. Similar contact angles are seen in micrograph (c) which shows another location where holes in the silicon film have just formed. We have seen numerous holes like these and observed also other contact angles, an example of which is shown in micrograph (d).

The contact angle between molten silicon and quartz is known to be⁴ 87°. The contact angle observed here is different because it is produced by the freezing of the molten silicon, which expands upon solidification, and by the stresses exerted on it by the oxide layers. The contact angle between Si and Si₃N₄ is known to be⁵ about 50°, indicating a better wetting of molten silicon to nitride than to oxide. The prevention of stripping caused by the interfacial nitrogen observed in the SIMS profiles, may therefore be a simple matter of better wetting provided by a thin nitride layer formed at the top SiO₂-Si interface.

We have also found that hydrogen affects the stripping. It was already discussed above that H_2 in the ambient caused smaller beads to form [Fig.3(c)]. A flow of H_2 was also impinged on a good sample during the course of its smooth crystallization and it caused stripping to occur immediately. These observations suggest that hydrogen may be the primary cause of the effect.

The hydrogen content of the CVD oxide film was measured by the resonant nuclear reaction⁶ of protons and ¹⁵N and it was found that a density of 0.5×10^{22} cm⁻³ of H atoms is approximately uniformly distributed in the oxide film (about 8% atomic ratio). This high H level was reduced, however, to below the background sensitivity of the technique ($< 0.02 \times 10^{22}$ cm⁻³) in a sample which was preheated in the oven to 1200 °C. It is possible that enough hydrogen remains in the oxide cap and it may diffuse to the silicon surface and deteriorate its wetting properties by saturating silicon bonds. Hydrogen gas may also permeate into the holes that open in the silicon film (as seen in Fig. 4), the hydrogen can then reach the bottom silicon surface and deteriorate the adhesion there as well; it can also provide pressure within the holes to further cause the silicon film to agglomerate into beads. In addition to improving the wetting, the role of the interfacial nitrogen may therefore be to prevent the hydrogen from deteriorating the silicon interface adhesion.

In summary the appearance and causes of the beading or stripping of the silicon film during its recrystallization have been investigated. SEM cross-section microscopy shows that the initial stage of bead formation occurs by holes forming in the silicon film with the top oxide layer remaining intact. The contact angles between the solidified silicon and the oxide layers indicate lack of wetting. The stripping was found to be enhanced in a H_2 -containing ambient which suggest the possibility that hydrogen in the CVD oxide film could contribute to this effect.

SIMS profiles of nitrogen through the capping layer have shown a good correlation between the occurrence of an N peak at the top SiO_2 -Si interface and the prevention of stripping. This interfacial nitrogen may be needed to improve the wetting between molten silicon and SiO_2 and possibly also to prevent hydrogen from further deteriorating the interface.

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