Al(Ge) metallization: The effect of Ge on the solubility of Si in Al

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The contact resistance between Al(Ge) alloys of various compositions and n^+Si has been measured using a four-terminal Kelvin probe. The samples processed for these measurements as well as similarly prepared thin films on unprocessed Si wafers have been characterized by both scanning and transmission electron microscopy after heat treatment in the temperature range 350–500 °C. The specific contact resistances for the alloys are comparable to those found for pure Al contacts to Si. However, the alloyed contacts show considerably more spiking into the Si substrate due to dissolution of Si in the metal layer. For temperatures around 350 °C, excessive spiking (compared to pure Al) is believed to be caused by increased solubility of Si in Al due to the presence of Ge. The reason for the enhanced solubility of Si in the alloy could be a counteraction of the strain in the Al lattice by Si and Ge. For anneals at 450 °C the extensive spiking could be associated with liquification of the contact metal.

The interaction between Al thin films and crystalline Si has been studied extensively due to the importance of Al as an ohmic contact to both n- and p-type Si.[1–3] Two major difficulties with the use of Al metallization are the well-known spiking and regrowth problems. Spiking into the Si substrate due to dissolution of Si in Al during sintering can be minimized by adding Si to Al to suppress the Si dissolution or by reducing the diffusion rate of Si in Al. The first solution is commonly used. The second approach has been investigated by Garg and co-workers who have measured the effects of small amounts of metal solutes in Al on the Al/Si interdiffusion.[4] They found that addition of In lowered the diffusion rate of Si in Al by about a factor of 2 but a much greater reduction is necessary in order to prevent spiking through shallow junctions. Neither solution solves the regrowth problem which manifests itself on cooling when the Al becomes supersaturated with Si which then precipitates within the metal layer as well as regrowing epitaxially at the Al/Si interface. This regrown Si p layer causes excessively high contact resistance to n-type Si.[5,6] Here, we report on the addition of Ge to Al as an approach to both the spiking and regrowth problems. In an aluminum solid solution the presence of a second dissolved element usually reduces the solubility of the first and vice versa.[7] To the best of our knowledge, the solid solubilities in the Al-Si-Ge ternary system have not been published and the effect of adding Ge to Al on the spiking can only be found through experiments. *A priori* one might think that a Ge-Al metallization would have some advantages over Si-Al when it comes to regrowth problems since if Ge precipitates out of the Ge-Al solid solution upon cooling and grows at the substrate interface a heterojunction will result. The electron barrier at the Al/Ge interface can then be expected to be lower than between Al/Si since the barrier height generally scales with the band gap. A low barrier height would then lead to a low ohmic contact resistance. A similar approach which takes advantage of the smaller Ge band gap is being evaluated by Robinson and co-workers.[8,9] They are looking at the suitability of a thin heavily doped epitaxial layer of Ge between Al and Si as a very low resistance ohmic contact.

We have tested our idea of adding Ge to the Al metal contact. However, the experimental results do not reveal the desired reduction in spiking. In this communication we briefly describe these results and an explanation for our findings.

Contact resistance measurements, scanning electron microscopy (SEM), and transmission electron microscopy were used to characterize Al(Ge) thin films with Ge concentrations from 2 to 75 at. %. Ge and Al were weighed out according to the desired alloy composition and placed in a W wire basket from which they were evaporated until the source material was exhausted. The total amount of Al evaporated was kept constant for all samples and the composition of the films was verified by Rutherford backscattering spectrometry. The pure Al films were about 3300 Å thick. Heat treatments were carried out in an argon atmosphere in the temperature range 350–500 °C for 1 h. Contact resistance measurements were made using Kelvin probes to n^+(100)Si.[10] The contact areas were about $10 \times 15\,\mu\text{m}^2$. The wafer processing steps were as follows: (1) standard chemical cleaning; (2) field oxide growth; (3) first-level masking (active area); field oxide etch and standard cleaning; (4) implantation of 5×10^{15} cm^{-2} As at energies from 100–200 keV; (5) standard chemical cleaning; (6) growth of 0.1-μm thermal oxide followed by a 30-min anneal under nitrogen at 950 °C; (7) second-level masking to open contact holes followed by an oxide etch down to Si; (8) 60-s etch in 50:1 H_2O:HF just prior to placement in an evaporator for metallization; (9) third-level masking to define metal pattern followed by chemical etching; and (10) anneals in argon as described above.

The Al (4% Ge) contact resistance data as a function of sintering temperature are shown in Fig. 1. The values are independent of temperature from 350–500 °C. Multiplication of the resistance values by the lithographic contact area yields a typical specific contact resistance of $2 \times 10^{-6}\ \Omega\ \text{cm}^2$

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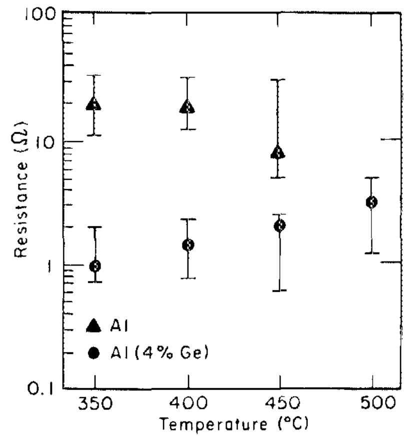

FIG. 1. Contact resistance of Al and Al (4% Ge) contacts as a function of sintering temperature.

which is the same as that found for good Al or Al(Si) contacts. The results for Al (2% Ge) contacts are similar with an average value of $5 \times 10^{-6}\ \Omega\ \mathrm{cm}^2$. Contact resistance values for Al(Si) had considerable spread which may be due to varying oxide thicknesses and/or etch rates across the Si wafers during processing. Also, the relatively large size of the contacts makes it more likely that there will be large resistance defects in the contact area. It is possible that the lower spread in the Al(Ge) resistance values could be related to the enhanced interaction between the alloys and the Si substrate as described below.

The SEM micrographs taken of the contacts are quite striking. Figures 2 and 3 contrast the Al vs Al (4% Ge) contacts annealed 1 h at 450 °C. All photos have been taken after the metallization has been removed using 9:1 HF. The pitting seen in Fig. 2 is typical for Al/Si contacts. In Fig. 3 the bright areas are Ge and the thinner lacy covering also contains Ge. The major feature is a huge crystallographic pit almost 3 μm deep which fills the entire contact opening. All Al(Ge) contacts observed are very similar to this one.

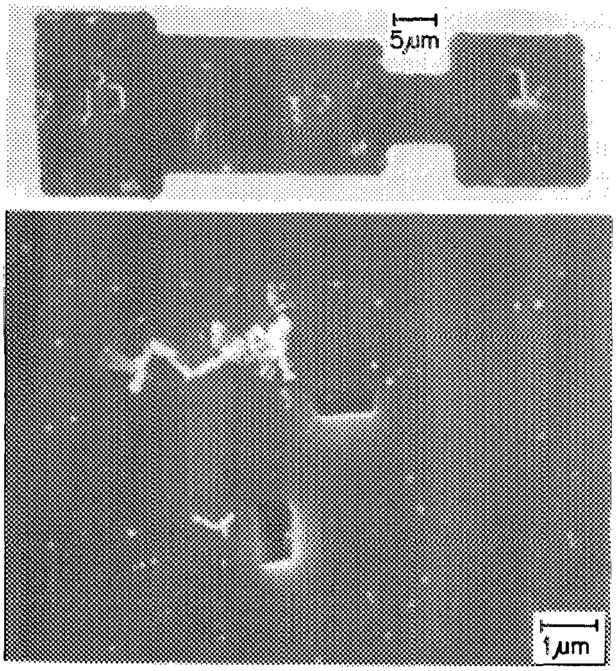

FIG. 2. (a) Ion implantation region of Kelvin probe showing three Al contacts after 1-h anneal at 450 °C with metallization removed; (b) closeup of center contact actually measured.

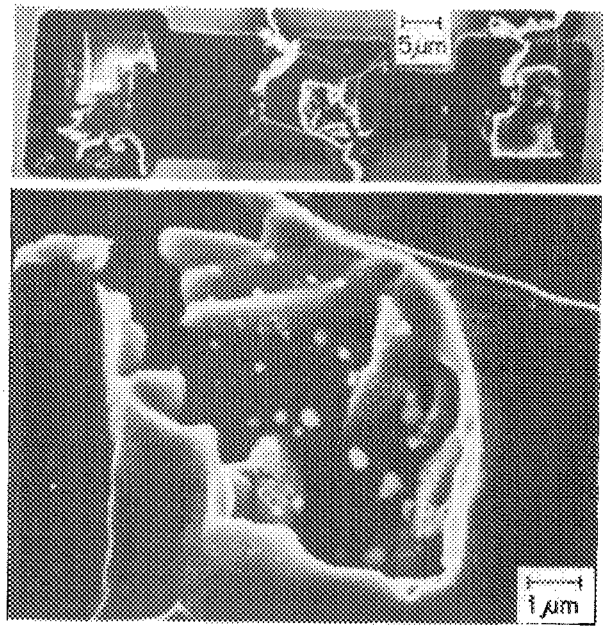

FIG. 3. (a) Ion implantation region of Kelvin probe showing three Al (4% Ge) contacts after 1-h anneal at 450 °C with metallization removed; (b) closeup of center contact actually measured.

In order to study the effect of varying the Ge concentration under identical surface conditions, a sample was prepared by evaporating Al, 4% Ge, and 30% Ge on the same wafer at the same time by using a shutter. Figures 4 and 5 show the 4% and 30% alloys, respectively, after a 1-h anneal at 450 °C. Both pictures reveal large Ge precipitates with thicknesses ranging from about 1500 Å to about 1 μm. The substrate of the 4% alloy sample appears quite porous. The amount of Si dissolved is very much greater than that found for the pure Al-on-Si sample. The substrate of the 30% Ge alloy sample shown in Fig. 5 appears almost glassy with a mildly undulating topography. There are many smaller pyramidal precipitates covering most of the surface. Both cross-sectional transmission electron microscopy and channeled Rutherford backscattering measurements show that the precipitates on both samples are polycrystalline. For both alloys the interface between the precipitate and the substrate is very uneven with many tangled dislocations. Transmission electron microscopy also revealed extensive pitting of the Al (4% Ge) sample as opposed to the larger scale roughness of the Al (30% Ge) substrate.

The difference in the appearance of the substrates of the 4% and 30% Ge samples may possibly be explained with reference to the Al-Ge phase diagram. The Al-Ge system has a eutectic temperature of 424 °C and reaches the eutectic composition at 30% Ge. At 450 °C the equilibrium state of an Al-Ge mixture containing 4% Ge would be a dual phase where most of the mixture is in the α (Ge dissolved in Al) phase and a small amount is in the liquid state.[11] Enhanced dissolution of Si into these small liquified areas may account for the porous appearance of the Si surface. In contrast the 30% Ge alloy is completely melted at 450 °C. This may be

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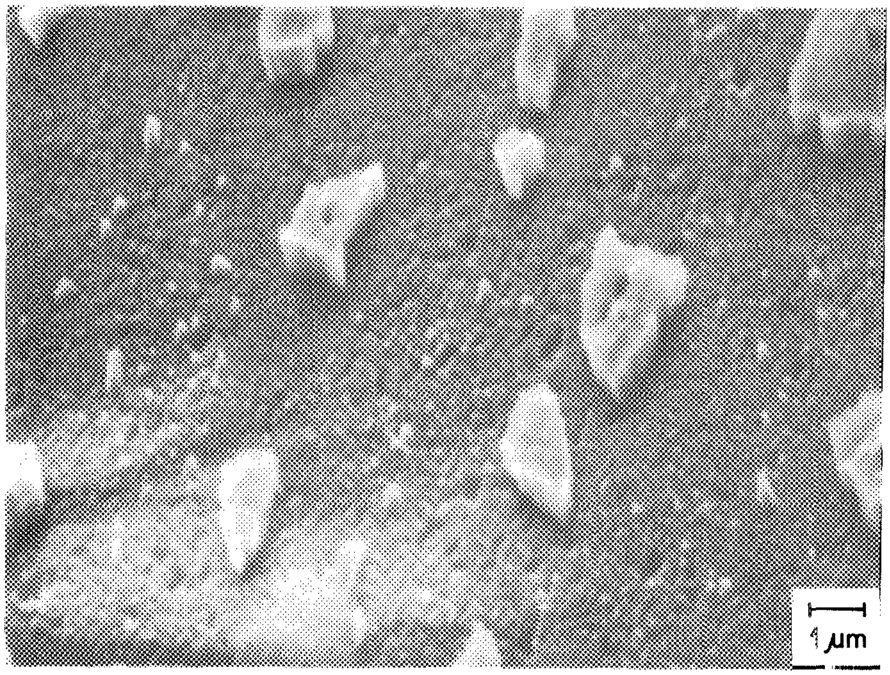

FIG. 4. Al (4% Ge) thin film on unprocessed Si substrate after 1-h anneal at 450 °C with the metal removed.

reflected by the rolling yet unpitted Si surface seen in these samples.

A sample prepared by evaporating Al (75% Ge) onto a (111) Si wafer and then annealing for 1 h at 450 °C was also examined using SEM with the metal removed. Even with such a large percentage of Ge, many large triangular pits measuring up to 2 μm on a side were seen. The Ge coverage was continuous although very pitted. In this case the equilibrium state at 450 °C would be a dual phase as in the Al (4% Ge) sample except that a much larger fraction of the alloy would be in the liquid state.

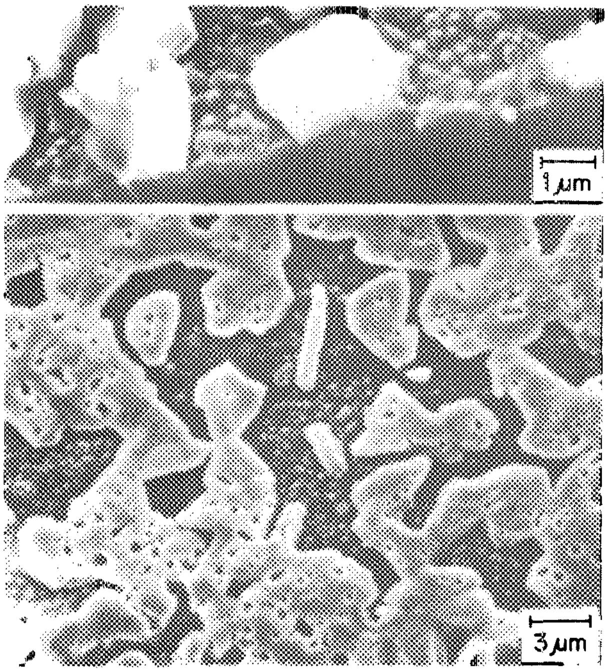

FIG. 5. Al (30% Ge) thin film on unprocessed Si substrate after 1-h anneal at 450 °C with the metal removed. The upper photo is a higher magnification sideview.

Annealing at 350 °C also results in considerably more pitting for the Al(Ge) alloys than for the samples with pure Al. In this case the explanation for the enhanced pitting cannot be due to dissolution of Si into the liquid state as suggested for annealing at 450 °C since we see no evidence for melting at 350 °C by SEM. We generally see the signatures of melting clearly in cases where we know it has occurred. Specifically, the Si surface of both the Al (4% Ge) and Al (30% Ge) samples were smooth and flat with isolated pits often located well away from the Ge precipitates. The Si surfaces show extensive modification and the appearances are quite distinct when Al/Si and Al-Ge/Si samples are annealed above the Al-Si eutectic at 577 °C and the Al-Ge eutectic at 424 °C, respectively. The signatures of melting are apparent both by SEM and visual inspection.

Another possible explanation for the extensive pitting (which would also apply at 450 °C for compositions other than at the eutectic) is that the solid solubility of Si in Al could be enhanced by the addition of Ge. Dissolution of Si in Al causes a volume contraction of 1.365×10^{-3}/at. % whereas Ge dissolved in Al causes a volume expansion of 1.115×10^{-3}/at. %.[12,13] At 350 °C about 1 at. % Ge dissolves in Al. Suppose we begin with Al (1% Ge) and assume that as Si is added the lattice contraction proceeds just as it would in pure Al except that now the initial lattice parameter is larger. In this case 0.95 at. % Si would be required to reach the same lattice parameter of a saturated solid solution of Si in Al at 350 °C. This is the same amount of Si that would normally dissolve at 525 °C. It may be reasonable to ignore all but lattice size effects on the solid solubility when the latter is limited so that direct interaction between solute atoms is small. Further, in the present case Ge and Si form a continuous series of solid solutions so they would not restrict one another's solubility in Al by forming a compound. If the

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solid solubility of Si in Al is increased this could lead to excessive spiking.

In summary, the 2% and 4% Ge in Al metallization schemes result in good reproducible contact resistance values from 350 to 500 °C. Still, the contacts are unsuitable for shallow junction applications because of the extensive spiking. At higher temperatures, this may be in part due to partial liquification of the Al(Ge) alloy. At 350 °C the enhanced solubility of Si in Ge may be due to the compensating effects of Si and Ge on the size of the Al lattice. Work is underway to quantify this effect.

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[13] The volume contraction is defined as $[a^3 - (a + \Delta a)^3]/a^3$ where a is the lattice parameter of Al and Δa is the change in the lattice parameter of Al due to the addition of 1 at. % solute.

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