DISPERSION STRENGTHENING OF AL FILMS BY OXYGEN ION IMPLANTATION

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ABSTRACT

Finely dispersed, stable Al-oxide particles were produced in Al films on Si substrates by oxygen ion implantation . A laser reflow technique was employed to vary the grain structure of some of the films. Transmission electron microscopy (TEM) was used to characterize the oxide particles and the grain size in the films, and a wafer curvature technique was employed to study the influence of microstructure on the deformation properties as a function of temperature.

For coarse grained laser reflowed films, ion implantation increased the strength considerably, both in compression and in tension. Weak beam TEM techniques showed that the strengthening is most likely caused by attractive interactions between dislocations and particles. As-deposited and ion implanted films showed a stable grain size of only 0.35 μm after annealing, which caused significant softening to occur in compression, especially at high temperature. However these films showed very high stresses in tension at temperatures below 130°C. In these films the presence of the oxide particles stabilizes the small grain size and this causes a weakening effect which can be attributed to diffusion controlled grain boundary relaxation mechanisms. The high tensile stresses at temperatures below 130°C can be explained by direct and indirect particle strengthening.

INTRODUCTION

Failure of Al interconnect lines severely limits the reliability of microelectronic devices. Many of these failures are related to insufficient mechanical strength of Al films. Thermal stresses caused by the difference in thermal expansion coefficient between the Al film and the substrate arise during high temperature steps of device fabrication. These stresses can relax by dislocation glide or by diffusion controlled deformation processes [1]. This can lead to hillock or void formation, and may result in short or open circuits.

Electromigration (E-M) is another important failure mechanism for conductor lines. Recent theories [2, 3] suggest that materials which can sustain higher stresses will show a better E-M resistance. Thus, the development of interconnect materials with higher mechanical strength is a promising way to improve reliability.

A well established method for strengthening bulk materials involves the formation of ordered precipitates or dispersoid particles, which act as obstacles to dislocation motion [4]. Precipitate forming Al(Si)-Cu alloys are already used in microelectronic devices. However, the precipitates in this system are not stable, because of the increasing solubility of Cu in Al with increasing temperature, and impart strengthening only at lower temperatures ($T<200°C$). To achieve a strengthening effect at all temperatures we have attempted to strengthen Al by creating a fine dispersion of stable Al_2O_3 particles.

Fine Al_2O_3 particles were created in sputter deposited Al films by oxygen ion implantation (OII). In order to separate the strengthening effect of dispersoids from those of grain boundaries, some of the Al films were subjected to a "laser reflow treatment" (LRT). Here the Al film is momentarily melted by a laser beam and after subsequent solidification [5] a large grain size is obtained. By combining oxygen ion implantation with laser reflow treatments, it was possible to study the effects of both Al_2O_3 dispersoids and grain size on the strength properties of Al films.

Transmission electron microscopy (TEM) was performed to study the microstructure of the films, and the strengths of the films were determined by substrate curvature measurements during thermal cycling.

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EXPERIMENTAL DETAILS

Al films 0.5 µm thick were magnetron sputtered onto unheated thermally oxidized (100) oriented silicon wafers 100 mm in diameter. The sputter system base pressure was 4.0×10^{-7} torr. The deposition rate was 1.8 nm/s at an Ar pressure of 3.0×10^{-3} torr.

The laser reflow treatment was done using an XMR 7100 system with a XeCl laser operating at 308 nm. The base pressure was 3.6×10^{-6} torr. The wafers were heated to 400°C prior to reflow. A laser energy dose of 3.2 J/cm^2 was used. The laser pulse duration was of the order of tens of nanoseconds.

The oxygen ion implantation was done using a Varian DF-4 ion implanter and was carried out in five partial implants, ranging in energy and dose from 10 keV to 190 keV and 5.0×10^{15} ions/cm^2 to 4.5×10^{16} ions/ cm^2, respectively, in order to achieve a relatively uniform oxygen concentration through the film. The final oxygen concentration is approximately 3.0 at%, corresponding to a maximum of 3 Vol% Al_2O_3.

To directly compare the effects of ion implantation and dispersion strengthening, films with four different kinds of treatment were studied: bare Al films (standard Al), films with a LRT (LR), films with only an OII (OII) and films with first a LRT and afterwards an OII (LR+OII). All of the Al films were unpassivated. Two samples of each kind were tested to confirm the results.

The film stress was measured as a function of temperature using the wafer curvature method [6] in which the curvature is measured by an optical lever. Every sample was subjected to 4 - 5 thermal cycles from room temperature to 480°C and back with a heating/cooling rate of 6°C/min. The TEM sample preparation was done as described in references 7, 8.

EXPERIMENTAL RESULTS

Strength Properties

Figures 1 and 2 show stress-temperature curves of the second thermal cycle of all of the four different process conditions. In Figure 1 the stress-temperature behaviors of the standard Al film and the OII film are compared and in Figure 2 those of the laser reflowed films (LR, LROII). All of the curves have a similar shape, indicative of the elastic and plastic processes that occur during thermal cycling. The thermal expansion coefficient of Al is higher than that of Si and so the stress in the film decreases,at first elastically, on heating. After the stress becomes compressive, the stress-temperature curve starts to deviate from the elastic line, indicative of plastic yielding. The same elastic-plastic sequence occurs on cooling.

The LR+OII films show the highest stresses, in both compression and tension. By comparison, the OII films show surprisingly low yield stresses in compression which decrease rapidly between 250°C and 480°C, though these films maintain very high stresses, comparable to those of the LR+OII films, in tension at low temperatures. Further, the strengthening effect observed in these films (OII) on cooling below 120°C is quite pronounced. The stresses in the LR films are slightly higher than in the standard Al films.

Microstructure

In order to understand the mechanical properties of these films it is necessary to know their microstructure. The grain structure of the films was determined by using light microscopy (LM), scanning electron microscopy (SEM) and TEM. The grain size after deposition was 0.6 µm and that after the laser reflow treatment was 5.6 µm. After the first thermal cycle, the following grain sizes were measured:

Process conditions	Grain size	Technique used
Standard Al film	1.4 µm	TEM
Oxygen ion implanted film (OII)	0.35 µm	TEM
Laser reflowed film (LR)	5.6 µm	LM, SEM
Laser reflowed and ion implanted film (LR+OII)	3.5 µm	LM, SEM

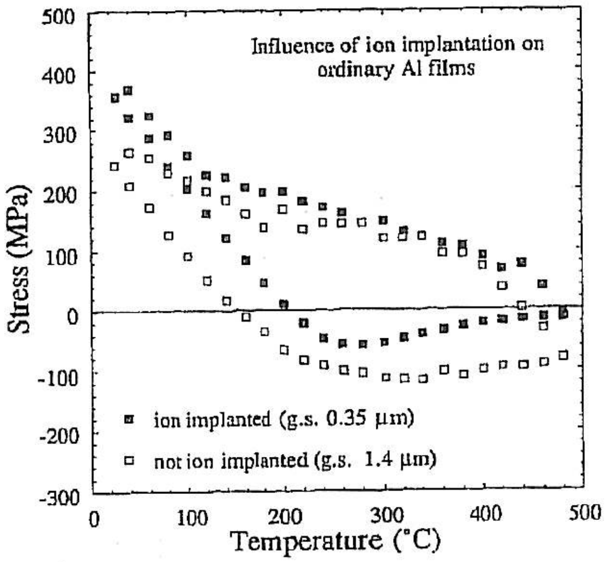

Fig. 1: Variation of stress with temperature for the second cycle of a standard Al film and an oxygen ion implanted (OII) film without laser reflow treatment.

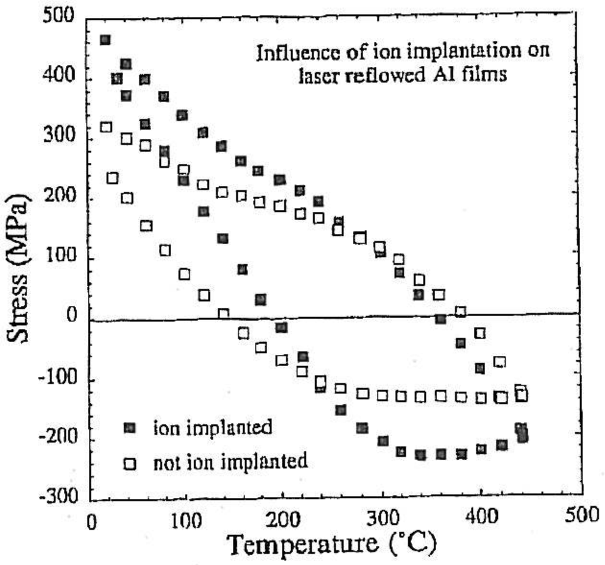

Fig. 2: Variation of stress with temperature for the second cycle of a laser reflowed (LR) film and a laser reflowed and oxygen ion implanted (LR+OII) film.

In subsequent thermal cycles, the grain size remained almost constant. In both kinds of oxygen ion implanted films (OII, LR+OII), the grain size is reduced by recrystallization during annealing as a result of the high defect density resulting from the oxygen ion implantation.

Figure 3 shows a bright field (BF) TEM micrograph of the microstructure after the first thermal cycle of a LR+OII film. Many so called "coffee bean" contrasts and Moiré patterns are visible in the micrograph. These "coffee bean" contrasts are caused by the strain fields of small particles in the Al matrix. The particle size is about 10 nm. The particles grow in subsequent annealing cycles and change their contrasts to small Moiré patterns. In addition, it was noted that particles also form at grain boundaries and grow preferentially there. Figure 3c shows the BF TEM micrograph of an OII film after the fourth cycle. The grain boundaries are densely decorated with particles and surrounded by particle-denuded zones. The particles at grain boundaries are mostly visible as black dots. Under suitable reflection conditions, 2 - 3 black and white stripes are visible inside the dots. Inside the grains one sees primarily small particles visible as "coffee bean" contrasts. The stable grain size of only 0.35 µm in these films suggests that the grain boundaries are pinned by the oxide particles. This pinning effect results in small recrystallized grains in the films with ion implantation.

SEM investigations were done to study the surface morphology and hillocking behavior of the films. The hillocking behavior of both kinds of films with the oxygen ion implantation treatment is significantly different from that of the films without the ion implantation treatment. After the first annealing cycle, the films with ion implantation (OII, LR+OII) show more and much larger hillocks than their counterparts without the ion implantation treatment. The LR films show the smallest amount of hillocks, followed by the LR+OII films and the standard Al films. The OII films show by far most hillocks.

Grain boundary grooving develops in the laser reflowed films (LR, LR+OII) during laser reflow processing and increases with further annealing. This grooving is especially pronounced in LR+OII films. In these films cavities form at triple points and small cracks develop along some grain boundaries. These damage processes are probably driven by the relatively high stresses in these films.

DISCUSSION

The LR+OII films show very high stresses in tension and compression (Fig. 2). In order to check whether dispersion strengthening is responsible for this effect, TEM investigations were done. Figure 3d shows a weak beam (111, 333)TEM micrograph of one of the LR+OII films. Dislocations pinned at particles are visible, indicating that dispersion strengthening indeed occurs. In the LR+OII films grain boundary diffusion related softening processes are not dominant because of the large grain size.

During cooling at low temperatures the slopes of the curves of both kinds of oxygen ion implanted films (OII, LR+OII) are almost equal to the elastic slope. This means that at low temperatures the yield strength is not reached. Especially in the ion implanted films without laser reflow treatment (OII), the transition from the region in which yielding occurs to the steep slope is very pronounced.

The OII films are very weak in compression (Fig. 1), especially at higher temperatures between 250°C and 480°C, where they show a considerable amount of softening. In addition, in tension above 300°C, they support stresses not higher than those of the standard Al films. The presence of stable particles in these films does not ensure high compressive strength at elevated temperatures. Instead, the small grain size of only 0.35 µm allows the stresses to be relaxed by diffusion controlled processes, in spite of the presence of the particles [8]. The high density of large hillocks supports this view. By contrast, dispersion strengthening is evident in tension below 120°C, most likely caused both directly by particle-dislocation interactions and indirectly by stabilizing a small grain size (Hall-Petch strengthening). Under 120°C, grain boundary diffusion controlled relaxation processes stop as shown by modelling the grain boundary diffusion controlled relaxation for the OII films [8].

The comparison of the hillock densities of the ion implanted films with and without laser reflow treatment shows that high stresses do not necessarily lead to extensive hillocking. Upon heating very high compressive stresses form in the LR+OII films, but only a few hillocks form on these films. In contrast, the OII films show very low compressive stresses but a high hillock density. The low stresses that are observed may be related to a high hillock density. Despite the high stresses in the LR+OII films, hillocks form at only a few of the grain boundaries. This suggests that special sites, such as specially oriented grains [9] and grain boundaries, are

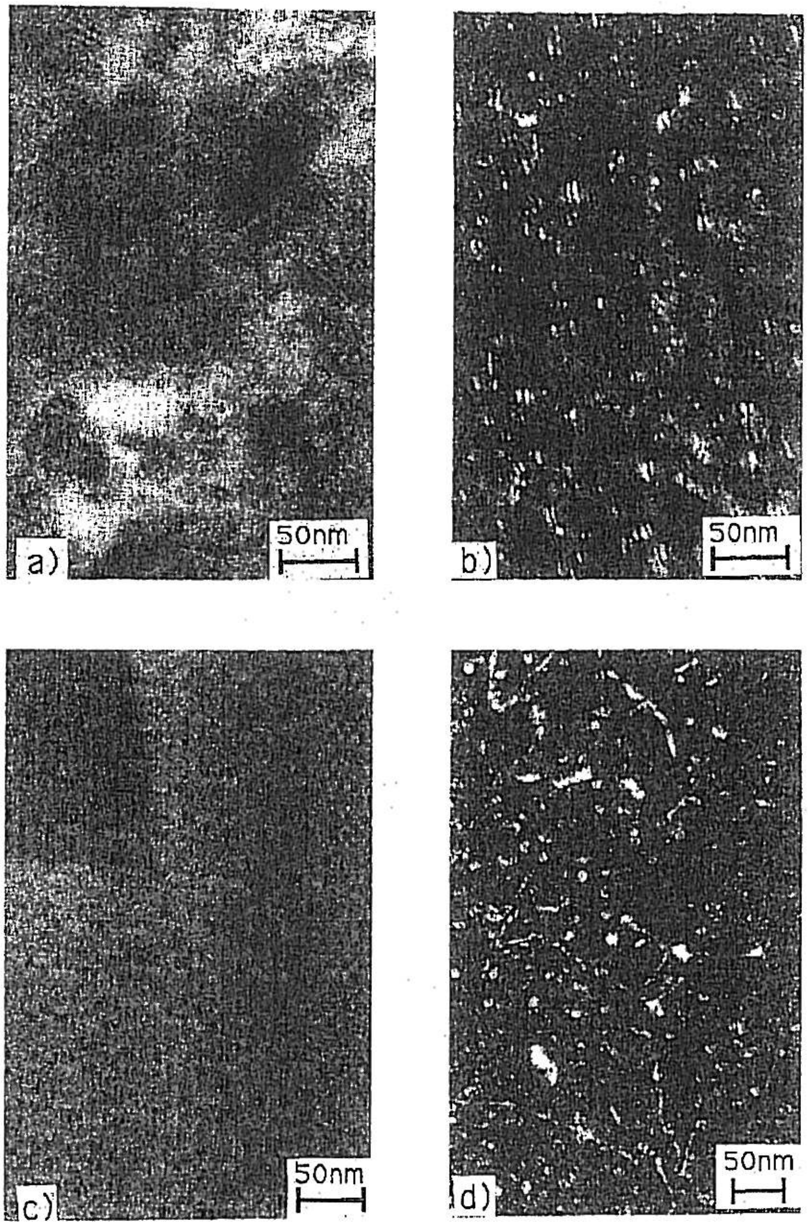

Fig. 3: Plan view TEM photograph of a) a LR+OII film after the 1st cycle; b) a LR+OII film after the 4th cycle; c) an OII film after the 4th cycle; d) weak beam (111, 333) TEM photograph of an LR+OII film after the 1st cycle.

necessary to form hillocks. In the OII films the grain size is smaller and the grain boundary density higher, resulting in a high density of specially oriented grain boundaries that can support hillock formation.

SUMMARY AND CONCLUSIONS

Oxygen ion implantation and coarsening by laser reflowing change the microstructure and the mechanical properties of Al films considerably:

1. After the first annealing cycle, very fine Al-oxide particles could be detected inside the grains and at the grain boundaries as well, where they grow preferentially. The particles grow in subsequent annealing cycles.
2. The particles at grain boundaries stabilize a very fine grain size of only 0.35 µm in the OII films which influences the mechanical properties considerably. These films show very low stresses in compression and extensive softening at higher temperatures. This can be attributed to diffusion-controlled stress relaxation mechanisms which are enhanced because of the small grain size. However, in tension at temperatures under 120°C, these films show very high stresses comparable to those of the laser reflowed and ion implanted films. Probably both direct (particle-dispersion interactions) and indirect (stabilized fine grains) particle strengthening cause these high tensile stresses.
3. High tensile and compressive stresses can be achieved only by particle hardening and grain coarsening (LR+OII). These stresses can be attributed to dispersion strengthening by dislocation-particle interactions.

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