EFFECTS OF Si IMPLANTATION ON Sb DIFFUSION IN Sb-SILICA SPIN-ON LAYERS

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ABSTRACT

The effects of Si implantation \((2 \times 10^{16} \text{ cm}^{-2})\) on the diffusion of Sb in Sb doped silica (SiO\(_2\)) spin-on layers and on their hardness were studied. RBS analysis and AES depth profiling showed that the implantation greatly retarded the Sb diffusion (1000-1200°C, 10 sec) in the oxide layer. Hence the high level of Sb near the SiO\(_2\)/Si interface, which is clearly seen for the unimplanted part of the sample, was not noticeable in the non implanted part. AES depth profile measurements also showed that the deposited oxide layers were more sputter resistant as a result of the implantation. The above observations are related to the ion induced radiation damage.

INTRODUCTION

In recent years, the application of spin-on glass (SOG) layers in the microelectronics industry has expanded with the increasing need for the miniaturization of devices and improvements in VLSI technology. Spin-on solutions either based on a siloxane polymer (1) or on a silicate base (2-4), dissolved in an alcohol solvent are most frequently used since the physical properties of the resulting films resemble those of thermal SiO\(_2\). The relative simplicity of production of spin-on layers as compared with standard techniques for thin film deposition such as CVD or thermal oxidation, has led to the extensive application of SOG in two areas: 1) As a method of planarization in the production of microelectronic devices (5,6) or as an insulating film between two metallic layers (7), 2) As a source for the diffusion of dopants into a semiconducting substrate (8,9).

In spite of the considerable interest in oxide layers based on spin-on technology, no research has been carried out, to our knowledge, on the changes induced by ion implantation into or through these layers. Previous research on thermal oxide layers or on quartz has shown that radiation damage strongly affects their physical properties inducing, for example, changes in the refractive index (10), or variations in the stress fields (11). To utilize the improved dielectric and mechanical properties of irradiated SOG films as well as to understand the behavior of impurities in the oxide layers, research on the effects of ion implantation into SOG is required.

In the present work the effects of \(^{28}\text{Si}\) implantation on various properties of Sb doped SiO\(_2\) spin-on films and on dopant diffusion was investigated. The objective of the study was to examine the influence of implantation on the Sb distribution profile and on the dopant mobility in the oxide layer after thermal treatment (short and long time heating). The penetration of the dopant into the Si substrate was also studied, and the results will be reported elsewhere.

EXPERIMENTAL

Silica films (Foulsimtone Comp.) doped with \(3 \times 10^{19} \text{ Sb cm}^{-3}\) were prepared on (111) Si wafers. The wafers were coated with wetting and the spin-on solution and spinning at angular velocities ranging from 1200 to

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3000 rpm for 15 sec. Hardening was obtained by heating to 200°C for 1 hr in air, yielding films 600-1500Å thick. The experiments reported here were carried out on silicon layers having a uniform thickness of 800Å as determined by RBS and Dektak measurements. After hardening, the wafers were cut into a number of pieces. One half of each sample was masked prior to implantation to the implantation dose as to permit direct comparison between the implanted and unimplanted parts. Si ions were implanted at 85 keV to a dose of 2x10^15 ions/cm². The implant energy and dose were selected such that the damage extended ~100Å beyond the interface, ensuring amorphization of the first interfacial region. The samples were divided into 3 groups: The first group was used to compare the bonding states in the implanted and unimplanted regions. IR spectroscopy was used to compare the bonding states in the implanted and unimplanted regions of the material.

The RBS and Auger electron spectroscopy (AES) were used to obtain qualitative information on the dopant concentration in the oxide layer in the implanted and unimplanted regions. AES was used to compare the bonding states in the implanted and unimplanted regions of the material. The AES backscattered Auger electrons into a surface barrier detector at an angle of 160°. The AES measurements were performed using a primary beam of 5 keV, 0.5μA electrons in a PHI 590A system. Depth profiles of the dopants were obtained using 1.5 keV Ar⁺ ion sputter etching with simultaneous monitoring of the peak-to-peak signal heights of the Auger transitions. IR measurements were carried out using a Perkin-Elmer spectrometer.

RESULTS

Comparison between implanted and unimplanted regions by the above techniques showed that a number of changes occur in the oxide layer as a result of ion implantation. In particular enhanced resistance to sputtering by Ar⁺ ions, and changes in the impurity profile after rapid thermal treatment were observed.

A significant reduction in out-diffusion of the impurity from the implanted SOG layer was also detected. In spite of these changes, the oxidation state of the antimony, as deduced from the Auger line shape, does not seem to have been affected by the implantation.

1. Hardness of the SOG layer

In order to assess layer hardness, its resistance to sputtering by Ar⁺ ions was monitored. An example which emphasizes the difference in sputter rate is shown in figure 1 in which the Auger signals of Si, O, and Sb are shown for an implanted (a) and unimplanted (b) sample. The sputter time required for the removal of the layer in the implanted region is substantially longer than in the corresponding unimplanted region. A series of measurements on layers with varying thicknesses (700-1500Å) showed that the sputter times for total removal of the layer of the implanted part were always 25 to 35% longer than those for the unimplanted regions. Similar results were obtained for arsenic containing spin-on layers.

In order to determine whether these differences are not the result of a real change in layer thickness induced by implantation, RBS, was employed. No such change could be observed, hence we conclude that the implanted SOG layer is 30% more sputter resistant than the as-deposited layer.

The reason for this change in sputter resistance was investigated by performing IR measurements on implanted and unimplanted regions. Although both regions showed the well known absorption line characteristic of SiO₂-Si bonds (12,13), a further group of lines, in the region of 3600 cm⁻¹, which were noticeable in the as-prepared film diminished as a result of the implantation. If we associate these lines with OH vibrations we speculate that some hydrogen is lost from the films as a result of the radiation damage, and hence the hardening of the film is increased. Indeed the effects that the amount of OH groups have on the hardness and density in silicon oxides have previously been reported (12).

2. Changes in impurity behaviour within the oxide layer

2-1 Impurity distribution

Comparison of the Auger depth profiles of Sb in the implanted and unimplanted rapid thermally treated layers showed drastic changes in the impurity distribution as a result of the implantation. An example of the Sb profile for a sample annealed at 1000°C for 10 sec is shown in figure 2. The profile of the unimplanted region (Fig. 2-a) shows that the annealing has left an impurity rich layer near the Silicon/Si Interface, while the surface region of the sample Ambient/Silica has lost about 60% of the dopant. This behaviour is typical of rapid thermally treated layers over a broad temperature range and indicates that the impurity tends to remain in the interfacial layer but is depleted from the region close to the surface.

In order to determine whether the impurity profile in the unimplanted layer following annealing was the result of normal diffusion as described by Fick's laws, the expected dopant distribution was calculated by solving the diffusion equation in the oxide layer (see Ref. 14 for analytical solutions). Such calculations were carried out for different values of the diffusion coefficient for antimony in SiO₂ in an attempt to reproduce the experimentally observed Sb profiles.
abnormally high concentration of a result of the Si implantation. dramatically different behaviour. In ~ 0.21 distribution is reached throughout the layer. This is in contrast to the measured profile where an abnormally high concentration of impurity is observed near the SiO/Si interface.

The profiles obtained from the implanted regions (Fig. 2-a) showed a dramatically different behaviour. In this case, the impurity distribution is relatively homogeneous and high throughout the layer. The Sb seems to be "locked in" the whole layer as a result of the Si implantation.

2-2 Impurity out-diffusion

The results of the AES measurements were used also to determine the amount of antimony in the layer after rapid thermal treatment at the temperature range 1000-1200°C. Figure 4 shows the total amount of Sb remaining in the oxides layer. In the implanted region this amount is almost temperature independent and close to the initial impurity level in the layer prior to thermal treatment. In the unimplanted region however, out-diffusion from the oxide layer, corresponding to approximately half the initial content was observed with a slight increase in out-diffusion at higher temperatures.

On the basis of the above results, an attempt was made to estimate the activation energy for diffusion of Sb in the silicon layer by integrating the total amount of antimony between the surface and a given depth in the oxide. In this estimate the abnormally high Sb concentration near the SiO/Si interface in the unimplanted sample was not taken into account.

A simple model based on diffusion from a slab with initial concentration \( C_0 \) into the vacuum was applied (15).

This model yields a closed expression for the integrated impurity concentration from the surface up to a depth \( h \), using the temperature dependence of the diffusion coefficient as:

\[
\frac{C}{C_0} = \frac{A}{B} e^{-E_a/KT} \exp[-A] \quad (1)
\]

Here \( A \) and \( B \) are constants determined by the parameters of the system. From Eq. 1:

\[
Y = \ln(A-B) - \ln E_a/\beta T \quad (2)
\]

Figure 5 shows the dependence of \( Y \) on \( 1/T \) for \( T=1000 \) and 5000 for the implanted and unimplanted regions.

The observed phenomena must be associated with radiation damage on other damage inducing processes, like electron or neutron irradiation, seem to have similar effects on vitreous silica or on thermal oxides (10,11). The observed hardening of SiO has been attributed to the tendency to harden the SiO layers and to minimize the bond strain, thereby leading to a reduction in structural stress. The damage caused by the Si implantation is much more severe than that of electrons or neutrons. Monte-Carlo simulations show that even at the high implantation doses used here (2x10^17 cm^-2), most bonds in the SiO layer have been disrupted at least once. It is therefore quite obvious that bond rearrangement and hydrogen loss has occurred, leading to the observed changes in the physical properties of the film. It is, however, interesting that in spite of the heavy damage to the film, the Sm diffusion was reduced. This is in contrast to known diffusion behaviour of most impurities in damaged crystalline materials where diffusion is enhanced by the presence of vacancies or interstitials.

The effects of ion implantation into, or through, SOG (doped or undoped) layers have, as well as future studies in which low temperature hardening of the films, or retention of the defects, is important.
The reason for the abnormally large impurity concentration near the interface of the unimplanted sample is not clear to us but may be associated with stresses at the SiO$_2$/Si interface (16). No major differences between fast and slow heat treatments were detected in the present experiments.

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REFERENCES


EFFECTS OF PRE-GATE OXIDATION INTRINSIC GETTERING UPON THIN GATE OXIDE INTEGRITY IN HIGH CARBON CONTENT CZ SI

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ABSTRACT

Effects of post-well drive intrinsic gettering (PWIG) upon the integrity of thin gate oxide in CZ Si wafers with carbon levels, $C_s$ ranged from 0.2 to 4 ppm were investigated. A 10 nm thick gate oxide capacitor was used to study its time-dependent breakdown characteristics and minority carrier lifetime. Our data have shown that PWIG cycles and/or carbon impurity affect both bulk oxygen precipitation and minority carrier lifetime, but not the oxide integrity.

INTRODUCTION

The continuing reduction of MOS device dimensions leads to a steady decrease in the thickness of gate oxide. Submicron MOSFETS and future generations of DRAM cells will require oxide films of the order of 10 nm [1,2]. As its thickness approaches as thin as 10 nm, the oxide is often subjected to a very high electric field. Due to the increase of electric field, a high quality thin gate oxide is essential to ensure the long-term reliability.

Recently, Yamabe et. al [3] have reported that surface contamination inadvertently added during various stages of device fabrication is the major cause of oxide defects. Intrinsic gettering (IG), which uses point defects associated with oxygen precipitation, is one of the schemes commonly used to getter these contaminants. In this study, we investigated one of the pre-gate oxidation wafer treatment processes "post-well drive intrinsic gettering (PWIG)" in a simulated CMOS process and studied their effects upon the time-dependent breakdown behavior of a 10 nm thick gate oxide in CZ Si wafers with carbon levels, $C_s$ ranged from 0.2 to 4 ppm.

EXPERIMENTAL

Characteristics of CZ Si wafers used in this study are listed in Table I. Thermal wave (TW) signals of these wafers after the standard two-step chemo-mechanical polishing process were measured by Therma-Probe 200. TW signal (which has been shown to influence the oxide breakdown characteristics and minority carrier lifetime [4]) ranged around 66 ± 3. Typical TW maps are shown in Fig. 1a and 1b. Before fabricating 10 nm gate oxide capacitor arrays, some of these wafers were subjected to a post-well drive intrinsic gettering (PWIG) cycle at 700°C in $N_2$ ambient for a time period ranging from 0 (NO PWIG) to 16 h to enhance the oxide nuclei density prior to the medium temperature