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Materials Science in Semiconductor Processing 9 (2006) 62–65

MATERIALS SCIENCE IN SEMICONDUCTOR PROCESSING

Diffusion profiles of low dosages chromium ions implanted into (1 0 0) crystalline silicon

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Abstract

Chromium ions with low dosages (1×10^{12} and $1\times10^{13}\,\mathrm{cm^{-2}}$) are implanted into silicon (1 0 0) crystalline substrates. Thermal anneals were carried out at different temperatures between 300 and 1000 °C to study the effects of ion implantation dose on the Cr diffusion profiles. Secondary ion mass spectrometry (SIMS) has been used to characterize the profiles of the Cr impurities. At $1\times10^{12}\,\mathrm{cm^{-2}}$ dosage and 500 °C anneal, the diffusivity of Cr in Silicon is determined to be $1.0\times10^{-14}\,\mathrm{cm^2\,s^{-1}}$.

Keywords: Cr; Si; SIMS; Diffusion; Ion implantation

1. Introduction

Diffusion of impurities in silicon has been studied extensively since the 1960s, primarily by the method of surface deposition followed by thermal anneals [1–3]. Because of the importance of silicon, a large body of data exists on the diffusion of dopants and impurities in silicon [4–6].

Of all metal impurities in silicon, the study of transition metal impurities in silicon plays a very important role, due to the fact that transition metal impurities are both major contaminants in silicon processing and fast diffusers in crystalline silicon. Major 3d transition metal contaminants in the silicon processing such as Fe [7,8], Ni [9,10] and Cu [11,12] have been extensively analyzed. But other 3d transition metal ions such as Cr and V are much less studied [13,14]. Recently, we have reported the diffusion profiles of high-dosage Cr and V ions implanted into silicon [15,16] by secondary ion mass spectrometry (SIMS). We found that the Cr profiles at high dosages and after thermal anneals were dominated by the amorphization of the silicon substrate through ion implantation and the subsequent solid-state-phase epitaxial growth of the amorphous layer.

As the implantation dosages drop below the amorphization threshold, no amorphous layer will be formed. The diffusion profiles after thermal anneals will be dominated by the interactions between the implanted Cr ions and the defects created by ion implantation. We expect the

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doi:10.1016/j.mssp.2006.01.010

diffusion profiles at low dosages would be different from the diffusion profiles at high dosages.

Here, we report the SIMS study of the diffusion profiles of low-dosage Cr implantation into crystalline (1 0 0) silicon substrates.

2. Experiments

Chromium ions were introduced into (1 0 0), p-type, B-doped CZ single crystalline silicon substrates by ion implantation at room temperature. The implantation was carried out at Implant Sciences Corporation. The implantation energy is 200 keV; the doses are 1×10^{13} and $1 \times 10^{12}\,\mathrm{cm}^{-2}$. Thermal treatments were carried out for the implanted samples at temperatures from 300 to 1000 °C, for 30 min each, and at temperatures of 500 °C for different time intervals (5, 10, 30 and 60 min). The annealing procedures were carried out using a Lindberg furnace with a long quartz tube. We first heated the furnace to a desired temperature. Once the desired temperature was reached, the quartz tube with the sample was placed in the center of the furnace. The annealing temperature was controlled within ±1 °C. A constant flow of high-purity (99.999%) Ar gas was maintained through the quartz tube during the annealing process. After completion of the anneal process, the quartz tube was removed from the furnace immediately, and the sample was cooled to room temperature with an argon flow.

SIMS was used to obtain depth profiles of the Cr impurities. The SIMS characterization was carried out at the UCF/Agere Materials Characterization Facility with a CAMECA IMS-3f using 100 nA O_2^+ primary beam at a source potential of 10 kV, an impact energy 5.5 keV and impact angle 40° from normal. The focused primary beam of oxygen ions was rastered over $200 \times 200\,\mu\mathrm{m}^2$ or $250 \times 250\,\mu\mathrm{m}^2$ areas, with detection of ions from an area of 60 μm diameter at the center of the raster. The sputtering rate is approximately 0.6 nm/s. The depth scale was established for each profile by measuring the crater depth with a stylus profilometer (Sloan Dektak IIA). The concentration was calibrated with the implantation dosages of the as-implanted samples and the measured erosion rate.

3. Results and discussion

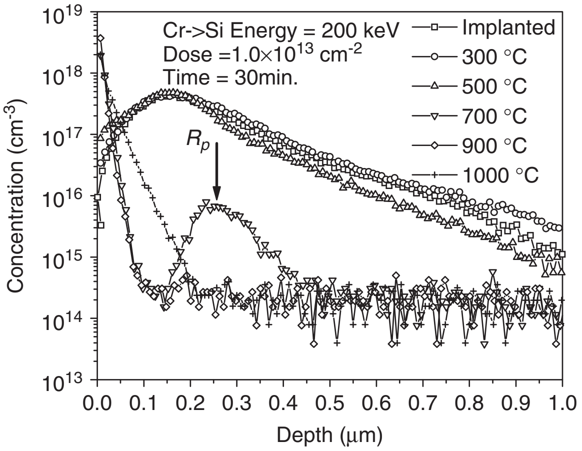

Fig. 1. SIMS depth profiles of 200 keV Cr, $1.0 \times 10^{13}\,\mathrm{cm}^{-2}$ implanted into Si and annealed for 30 min in Ar gas.

In Fig. 1, SIMS profiles of the 200 keV Cr, $1 \times 10^{13}\,\mathrm{cm}^{-2}$ implanted and annealed samples are presented. At 300 °C anneal, Cr impurities started to diffuse slightly into the substrate. After annealing at 500 °C a contraction behavior appeared. This is suggested to be a result of Cr clustering reactions. The depth profile of the 700 °C-annealed sample showed a peak at the implantation projection range R_p. It is not clear whether this peak is the result of Cr clusters or is caused by defects near the projected range of the ion implantation. At 900 °C, the peak is not present and most of the Cr atoms were in the top 0.1 μm layer near the surface, and a significant amount of the implanted Cr ions were evaporated during annealing. At 1000 °C, the diffusion profile showed that the out-diffusion of Cr atoms seems to slow down compared with the 900 °C profile. This slowdown in the movement of Cr ions could be due to surface oxygen diffusion into the Si substrate at this high temperature.

In Fig. 2, SIMS profiles of the 200 keV Cr, $1 \times 10^{12}\,\mathrm{cm}^{-2}$ as-implanted and annealed samples, are presented. Compared with the samples implanted with higher dosages [15,16] there are fewer extended defects in the 200 keV Cr, $1 \times 10^{12}\,\mathrm{cm}^{-2}$ implanted sample. At 300 °C, the profile remains the same. At 500 °C, the redistribution is similar to normal diffusion. However, at 700 °C most of the Cr impurities are driven to the surface, and there is no Cr peak at 0.26 μm. This suggested that the $1 \times 10^{12}\,\mathrm{cm}^{-2}$ dosage of Cr it will not be expected to have a large number of defects. One can see that Cr impurities are easy to evaporate via the silicon surface. At 900 °C, Cr ions were all driven to the top 0.1 μm of the surface region. This Cr profile is

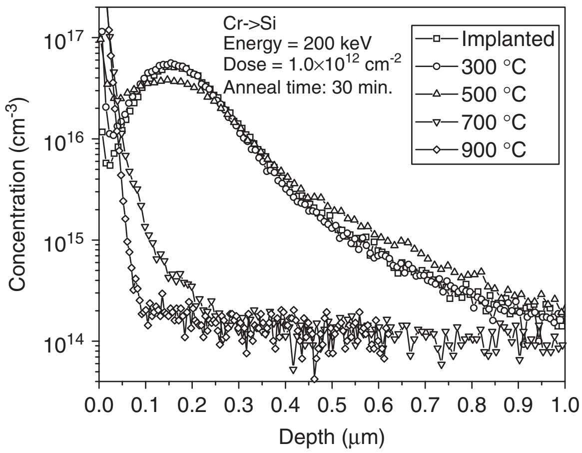

Fig. 2. SIMS depth profiles of 200 keV Cr, $1.0\times10^{12}\,\mathrm{cm}^{-2}$ implanted into Si and annealed for 30 min in Ar gas.

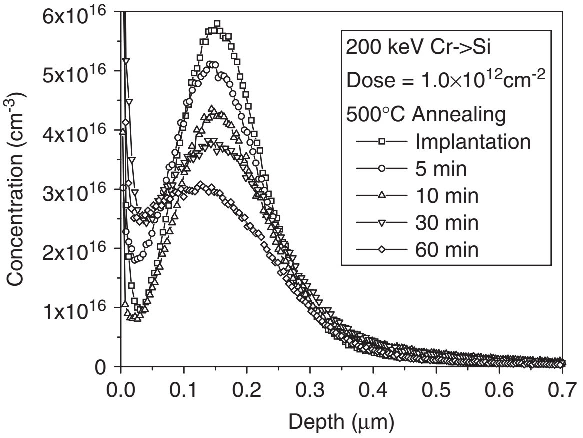

Fig. 3. SIMS depth profiles of 200 keV Cr, $1.0\times10^{12}\,\mathrm{cm}^{-2}$ implanted into Si and annealed at 500 °C for different annealing times.

almost the same as that of the $1\times10^{13}\,\mathrm{cm}^{-2}$ dosage after 900 °C anneal.

From the above results it becomes clear to us that at low dosage there are fewer implantation-induced defects generated to mask or alter the expected simple diffusion behavior. At this low dosage, it is possible to obtain Cr diffusivity data for the silicon substrate. We took the $1\times10^{12}\,\mathrm{cm}^{-2}$ Cr-implanted samples and annealed them at 500 °C with time intervals between 5 and 60 min. The SIMS-measured Cr depth profiles are shown in Fig. 3. Here, we can see the gradual broadening of the full-width at half-maximum and the gradual decrease in the maximum intensity signaling a "simple" diffusion.

We fit this as-implanted Cr distribution with the solution to the "simple" diffusion equation:

$$\frac{\partial C(x,t)}{\partial t} = D\,\frac{\partial^2 C(x,t)}{\partial x^2}. \tag{1}$$

We ignored the surface 50 nm Cr distribution in our fit. The result of the fit is used to simulate the diffusion profiles at different annealing times. The simulated profiles with a diffusivity of $1.0\times10^{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ are shown in Fig. 4. The diffusivity obtained does not agree with previous reported measurements [17–19]. However, in view of the B-doping in our silicon substrate, our value should be compared with the Cr diffusivity of $2\times10^{-17}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ measured at room temperature [20] in a B-doped, edge-defined, film-fed, grown polycrystalline silicon substrate. At present, the measured low diffusivity of $1\times10\mathrm{E}{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ cannot be explained satisfactorily.

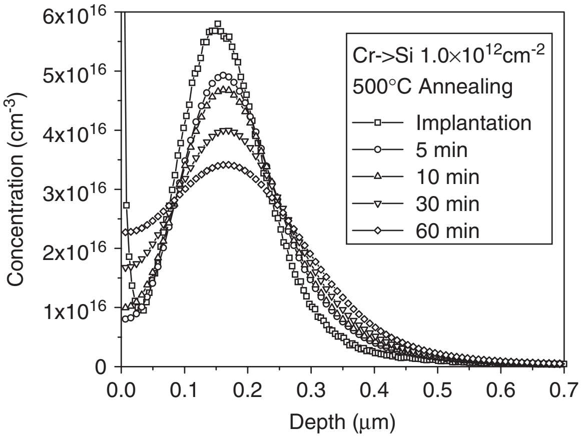

Fig. 4. Numerical simulation results for the 200 keV Cr, $1.0\times10^{12}\,\mathrm{cm}^{-2}$ implanted into Si and annealed at 500 °C for different times. Diffusivity of $1.0\times10^{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ is used in the simulation.

4. Conclusions

Secondary ion mass spectrometry has been employed to study the diffusion behavior of implanted Cr ions in crystalline silicon. At $1\times10^{13}\,\mathrm{cm}^{-2}$ dosage and, after thermal anneals, the main features in the Cr profiles are affected by: (1) the damages created by ion implantation, (2) surface traps, and (3) the low solubility of Cr in silicon. At $1\times10^{12}\,\mathrm{cm}^{-2}$ dosage, the Cr diffusivity at 500 °C is determined to be $1\times10^{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. This low value of diffusivity of Cr in silicon at 500 °C could be due to: (1) Cr–B interaction, (2) Cr–vacancy interaction, or (3) Cr–Si(interstitials) reaction/dissociation. Further investigations are needed to resolve this issue.

Acknowledgment

The authors acknowledge technical support from the Materials Characterization Facility (MCF) at University of Central Florida.

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