Use of ultrasound for metal cluster engineering in ion implanted silicon oxide

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This letter presents an approach to metal cluster engineering in silicon oxide that uses ultrasound vibration applied *in situ* during implantation. Analysis by transmission electron microscopy has demonstrated that *in situ* applied acoustic vibrations result in a lowering of the clustering threshold and an increase in cluster size after subsequent annealing. The results are interpreted in terms of the interaction between ultrasonic vibrations and point defects leading to the formation of vacancy-rich regions, as determined by deuterium decoration method. The excess of vacancies in the precipitation region facilitates nucleation and stimulates cluster growth due to enhanced diffusion of metal species. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2430055]

Metal nanoclusters fabricated by ion implantation in silicon dioxide have been a subject of numerous investigations due to their potential application in optoelectronic devices.[1,2] Until now, studies on the formation and growth kinetics of metal nanoparticles in silica have been mainly concentrated on the influence of ion dose, dose rate, substrate, and implant temperature. However, little is known about the effect of ultrasonic waves propagating in the solid during ion implantation. In our previous work, we have already shown that *in situ* applied ultrasonic treatment (UST) during implantation of silver in silica leads to increased precipitate size after postimplantation annealing.[3] The physical mechanism of this effect was discussed in terms of enhanced diffusion of silver due to the accumulation of vacancies in the precipitation region. However, more extensive experimental support for the proposed model is necessary.

A commonly accepted procedure for the experimental determination of point defects and defect clusters produced by ion implantation is the so-called impurity decoration method. The decoration is frequently done by introducing gold or copper followed by annealing, which results in the redistribution and gettering of decoration impurity on defects.[4,5] Recently proposed defect decoration by hydrogen/deuterium produced in low temperature plasmas has the advantage of effective trapping of hydrogen on defects and high hydrogen mobility even at low temperatures, making this approach very attractive for the accurate determination of defect distributions.[6]

In the present letter we investigate in detail the effect of *in situ* applied ultrasound waves on the nucleation and growth kinetics of copper clusters. The cluster formation process was studied by high resolution transmission electron microscopy (TEM). The spatial distribution of defects was investigated by means of the deuterium decoration method and analyzed with secondary ion mass spectrometry (SIMS).

In our experiments boron-doped (100) silicon was oxidized in a vertical furnace at 1000 °C in oxygen atmosphere. The final oxide thickness was 100 nm, as determined by spectroscopic ellipsometry. The samples were implanted with 50 keV copper ions at different doses from 1×10^{15} to 5×10^{15} cm^{-2} keeping ion current density constant at 0.2 μA/cm^{-2}. The ultrasound vibrations were generated in the sample during the implantation process by an ac driven piezoelectric transducer operating in resonance vibration mode at a frequency of 9 MHz and an acoustic power of 1 W cm^{-2}. The resulting mechanical deformation was equal to 4×10^{-6}. The samples were finally annealed in vacuum at 700 °C for 20 min.

Figure 1 shows ^{63}Cu SIMS depth profiles after annealing in samples implanted with an ion dose of 1×10^{15} cm^{-2} with (filled symbols) and without *in situ* applied UST (open symbols). Both samples are characterized by a pronounced trapping of copper on the SiO_2/Si interface, an effect that was previously discussed by Bai *et al.*[7] In the figure, we can also see the distribution of target vacancies calculated using SRIM

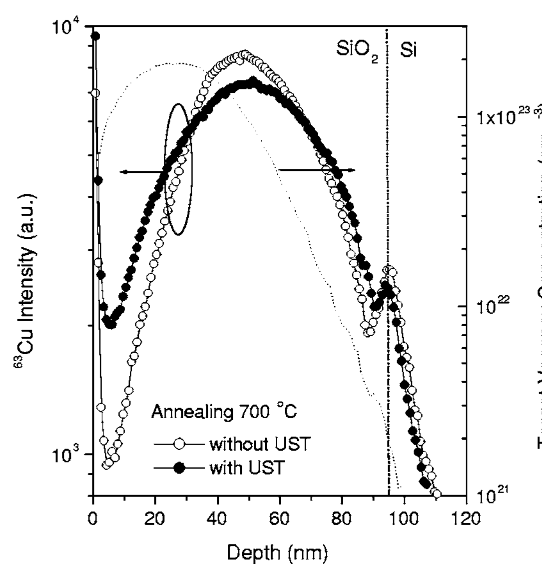

FIG. 1. SIMS ^{63}Cu depth profiles in Cu-implanted SiO_2 (50 keV, 1×10^{15} cm^{-2}) after annealing at 700 °C for 20 min in vacuum. The open symbols represent the case of implantation without ultrasound and the filled symbols represent the case of implantation with *in situ* applied ultrasonic vibrations. The calculated distribution of generated vacancies is shown with a dotted line.

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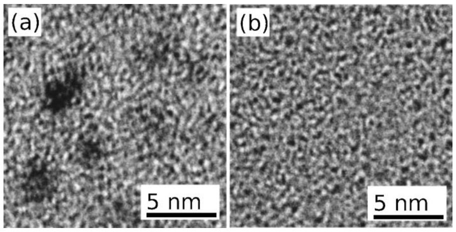

FIG. 2. Cross-sectional TEM views of samples implanted with *in situ* applied ultrasonic vibrations (a) and without (b) to a dose of 1×10^{15} cm^{-2} after annealing at 700 °C for 20 min in vacuum.

(stopping and range of ions in matter) software.[8] In the near surface region down to 30 nm, where the vacancy distribution reaches its maximum value, a higher Cu concentration is observed in the case of implantation with *in situ* applied ultrasound. Corresponding cross-sectional TEM micrographs taken in the near surface region on samples implanted with and without *in situ* applied UST are depicted in Figs. 2(a) and 2(b). As can be seen, the sample implanted without ultrasound is almost featureless, whereas *in situ* applied acoustic vibrations result in the formation of small (<2 nm) precipitates identified by analysis of electron diffraction patterns as fcc Cu. This observation indicates a distinctly lower clustering threshold in the case of implantation with *in situ* applied UST and can be explained by a high concentration of vacancies created in the precipitation region, a conclusion supported by calculations of Vanhellemont and Claeys.[9] Further evolution of cluster growth with an increase of implantation dose in samples implanted with and without applied UST is shown in Figs. 3(a) and 3(b), respectively. Almost spherical Cu clusters are present in both samples; however, the sample implanted with applied ultrasound is characterized by an increased cluster diameter and a broader size distribution. Since the particle growth is a diffusion driven process and diffusion of metals in dielectrics is often governed by vacancy-assisted mechanism, it is safe to assume the formation of a vacancy supersaturation region in the case of implantation with applied ultrasound.

In order to prove this idea, the oxide films were implanted with argon, well known for its ability to produce large amount of vacancies and vacancy complexes.[10] The argon was implanted with an energy of 40 keV at a dose of 1×10^{14} cm^{-2} with current density less than 0.2 μA/cm^{-2}. The samples were then exposed to a low temperature deuterium rf plasma (30 W, 0.02 mbar) for 40 min, as described in Ref. 6. In order to enhance deuterium indiffusion the substrates were kept at 200 °C during plasma exposure. In Fig. 4, the measured deuterium depth profiles in samples implanted with (filled symbols) and without applied UST (open symbols). The distribution of generated target vacancies is shown with a dotted line. As can be seen, in the case of implantation with ultrasound, deuterium is trapped in two zones: (i) near surface region and (ii) SiO_2/Si interface. It is also apparent that the concentration of deuterium in the sample implanted with ultrasound is noticeably higher than in the normally implanted sample. The difference is more pronounced on the SiO_2/Si interface and in the region of maximum accumulation of vacancies. Taking into account that atomic hydrogen effectively getters on defects, one can infer that *in situ* applied ultrasonic vibrations result in a higher generation rate of vacancy-interstitial pairs, as previously discussed by Ostrovskii and Lysenko.[11] In order to identify the nature of defects in these two regions, the sample after plasma treatment was heated to 450 °C for 20 min using the property of deuterium to be bound more strongly to vacancies than to interstitial-type defects.[6] The resulting profile is shown in Fig. 4 with a solid line. One can see that the concentration of deuterium on SiO_2/Si interface is reduced, whereas in the region of maximum vacancy distribution, its concentration differs only slightly from the initial one. This observation unequivocally confirms the accumulation of interstitials on the SiO_2/Si interface and the creation of vacancy excess in the near surface region.

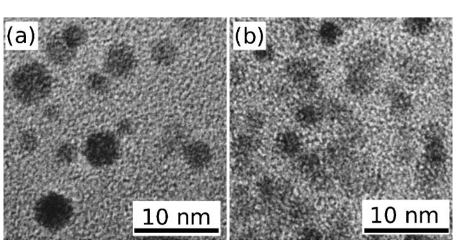

FIG. 3. Cross-sectional TEM views of samples implanted with *in situ* applied ultrasonic vibrations (a) and without (b) to a dose of 5×10^{15} cm^{-2} after annealing at 700 °C for 20 min in vacuum.

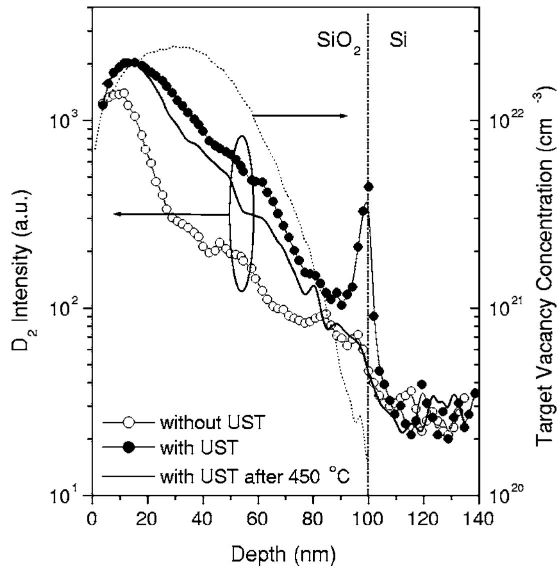

FIG. 4. Deuterium SIMS profiles in Ar-implanted SiO_2 at 40 keV and a dose of 1×10^{14} cm^{-2} without acoustic vibrations (open symbols) and with *in situ* applied ultrasound (filled symbols) after exposure of the samples to a low temperature deuterium plasma. The calculated distribution of generated vacancies is shown with a dotted line. The evolution of the deuterium profile after annealing the ultrasonically implanted sample at 450 °C is shown with a solid line.

According to the calculations of Krevchik *et al.*[12] who studied impurity diffusion in silicon under the action of weak acoustic fields, the low amplitude (mechanical deformation of $10^{-5}-10^{-6}$) ultrasound vibrations disturb the equilibrium state of the phonon subsystem, which results in energy exchange between nonequilibrium phonons and impurity atoms, thus decreasing the activation energy of impurity migration. We suggest that similar considerations could be applied for point defects and defect complexes. Ultrasound waves interacting with the excess interstitials generated during ion implantation could promote the decrease of the activation energy of interstitials migration, thus enhancing their diffusion toward silicon oxide/silicon interface. It is conceivable that remaining vacancies form complexes by ripening mechanism.[13] These complexes are, in general, immobile even at high temperatures. This is, however, a point open to discussion and will be further investigated in the future.

In conclusion, we have performed Cu implantation at several doses $(1\times10^{15}-5\times10^{15}\ \mathrm{cm}^{-2})$ in silicon oxide under the action of an acoustic field. We have shown that *in situ* applied ultrasound vibrations result in the lowering of the copper precipitation threshold and an increase of the precipitate size after postimplantation annealing. The physical mechanism of this effect is attributed to the enhanced diffusion of generated interstitials and the accumulation of vacancies in the precipitation region, as demonstrated by deuterium decoration method.

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