Influence of *in situ* ultrasound treatment during ion implantation on formation of silver nanoparticles in silica

Andriy Romanyuk[a)]
Institute of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland

Vladislav Spassov
Swiss Center for Electronics and Microtechnology, Rue Jaquet-Droz 1, 2007 Neuchatel, Switzerland

Viktor Melnik
IHP-Microelectronics, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany

(Received 12 August 2005; accepted 6 January 2006; published online 15 February 2006)

We report on the effect of *in situ* ultrasound treatment on the clustering process of silver atoms in ion-implanted SiO_2. Cross-sectional transmission electron microscopy shows single-crystal Ag spheres with an increased cluster size when prepared using ultrasound vibrations. Time-of-flight secondary-ion-mass spectrometry demonstrates an enhanced yield of $[Ag_2]^{216}$ complexes in structures treated with acoustic waves. An analysis of the influence of ultrasound on defect reaction kinetics as well as on different stages of the clustering process is performed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2171773]

I. INTRODUCTION

Nanostructured metal-insulator composites possess fascinating electromagnetic properties which differ greatly from those of ordinary bulk material. Large third-order nonlinear susceptibility and fast time response near the surface plasmon resonance frequency make them promising candidates for application in many optoelectronic components.[1–3] Ion implantation is one of the suitable techniques for the synthesis of nanoparticles in dielectric matrices due to its high degree of controllability of dopant concentration and space distribution.[4] Another important advantage of the technique is the possibility of extending elemental cluster-forming compounds and alloys using sequential implantation of different ions.[5,6]

Physical characteristics of metal-insulator composites are governed by the shape, size, and size distribution of nanoparticles which are determined by thermodynamic conditions during the ion implantation and subsequent annealing. The formation of silver nanoparticles in silica by ion implantation has been extensively studied before.[7–9] Numerous publications have mainly concentrated on the influence of ion dose, dose rate, and substrate and implant temperatures on cluster formation and growth kinetics.

It has been suggested that ultrasound waves propagating through the solid can affect the generation and motion of point defects, leading to different defect reactions.[10,11] Krüger *et al.*[12] reported on enhanced amorphization of silicon during argon implantation using *in situ* ultrasound treatment (UST). The influence of ultrasound is discussed in terms of its interaction with point defects and ultrasonic-stimulated enhanced diffusion of interstitials. A review on ultrasound-stimulated processes in semiconductors has been published, demonstrating enhanced diffusion of atomic hydrogen in thin polycrystalline Si films and improved homogeneity of recombination and transport properties.[13]

In this work we report on the influence of *in situ* applied ultrasound waves during the implantation of silver into thermally grown SiO_2. Ultrasonically induced lattice excitations result in trigged defect reactions in silica, influencing the impurity diffusion processes and consequently the clustering kinetics. We observed a pronounced increase in the Ag cluster diameter upon the action of *in situ* applied acoustic field. A model that takes into account ultrasonically stimulated enhanced diffusion of interstitials and accumulation of vacancies in the ion projected range region is proposed.

II. EXPERIMENTS

Thin silicon oxide films were grown on B-doped Cz–Si (100) wafers in a dry oxygen atmosphere at 1150 °C in a vertical furnace (details are described elsewhere[14]). The thickness of the silica film comprised 100 nm as determined by spectroscopic ellipsometry. The samples were implanted with 40 keV Ag^+ ions, keeping the ion flux constant at 3.0×10^{11} cm^{-2} s^{-1}. The ion dose was 3.0×10^{15} ions/cm^2 for all experiments. The implantation was performed at room temperature.

Low-amplitude ultrasonic vibrations were generated in the sample by operating the transducer in a resonance vibration mode at a resonance frequency of 5 MHz and acoustic power of 1 W cm^{-2}. The ion-implanted samples were then annealed in vacuum at 550 °C for 20 min. Microstructural characterization, i.e., the cluster sizes, size distributions, and number densities, was investigated with Philips CM 200 transmission electron microscope operating at a 200 kV accelerating voltage, equipped with an energy dispersive x-ray analysis (EDAX) spectrometer. Low-energy time-of-flight secondary-ion-mass spectrometry (ToF-SIMS) depth profiling was performed with a ToF-SIMS IV system in dual beam mode with 1.0 keV Cs^+ sputtering and 10 keV Ar^+ primary-ion beam for secondary-ion generation.

[a)]Electronic mail: andriy.romanyuk@unibas.ch

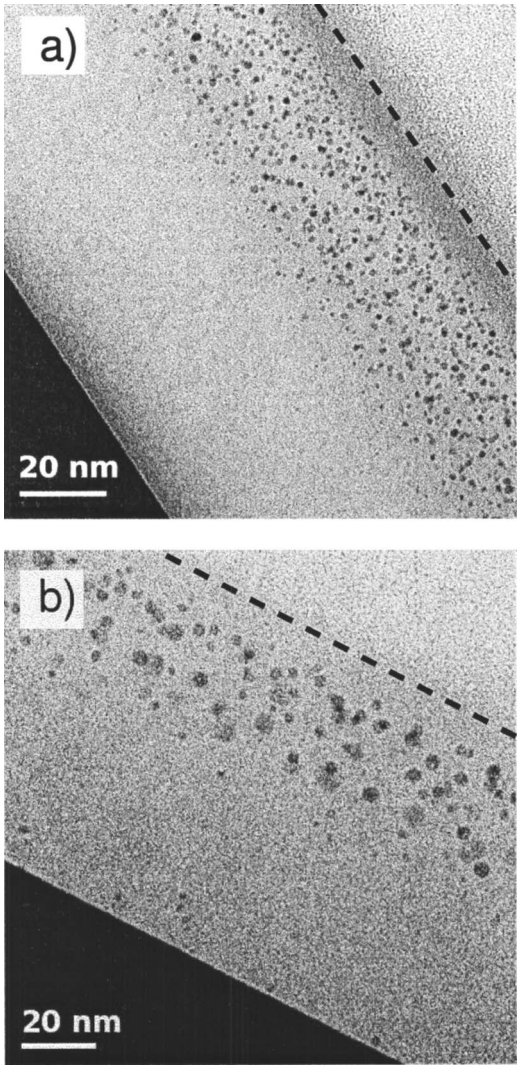

FIG. 1. Cross-sectional bright field TEM views of Ag-implanted SiO_2 at 3.0×10^{15} ions/cm^2, 40 keV, annealed in vacuum at 550 °C without UST (a) and with *in situ* applied UST of 5 MHz (b). The dashed lines denote the surface position.

III. RESULTS

Figure 1(a) shows the cross-sectional bright field transmission electron microscopy (TEM) image of a Ag-implanted sample without UST after annealing at 550 °C. The particles are mostly spherical in shape and distributed within a region of ~10–60 nm from the surface. Analysis of electron-diffraction rings and dark field images (not shown here) has verified that the Ag clusters are fcc single crystals, randomly oriented. At the same time *in situ* induced ultrasonic vibrations led to the formation of Ag clusters with substantially increased diameter [Fig. 1(b)].

The remarkable difference in size distribution is best shown in Fig. 2 where the average cluster diameter after analysis of TEM micrographs is plotted. The shift of the average cluster size towards higher values and the corresponding broadening of the cluster size distribution upon the action of applied acoustic field are evident. The results of the TEM analysis give average cluster diameters of $\langle D\rangle_{\mathrm{UST}}=3.34\pm0.7$ nm and $\langle D\rangle_{\mathrm{normal}}=1.9\pm0.34$ nm for the samples implanted with and without UST, respectively.

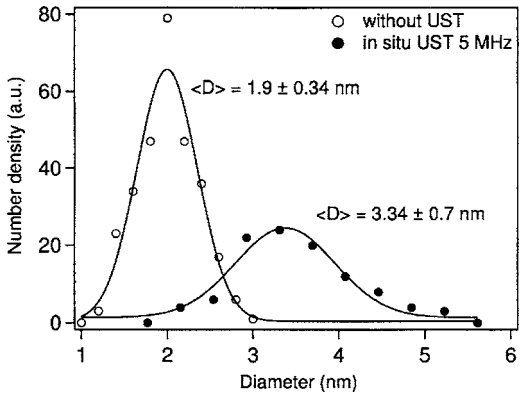

FIG. 2. Average cluster diameter of Ag-implanted SiO_2 at 3.0×10^{15} ions/cm^2, 40 keV, annealed in vacuum at 550 °C without UST (open symbols) and with *in situ* applied UST of 5 MHz (filled symbols).

Figure 3 depicts ToF-SIMS depth profiles of $[Ag_2]^{216}$ fragment ions in samples implanted with UST (open circles) and without UST (filled circles) after annealing at 550 °C. The measured distributions are close to a Gaussian profile with a centroid located at ~25 nm and a straggling tail which is limited to ~50 nm. The yield of $[Ag_2]^{216}$ fragment ions in the sample implanted with applied acoustic waves shows an increase in intensity, whereas the yield of Ag^{107} remains the same for both samples (not shown here). Generally, an ion yield depends on many factors such as an atom's chemical environment, structure of the analyzed material, physical roughness of the surface, etc. Taking into account that all parameters for both samples are the same except the particle size, (Fig. 1) one can infer that the difference in the yield of $[Ag_2]^{216}$ fragment ions is associated with the structure of the clusters and points to the fact that the implanted silver is present in clusters whose sizes are bigger than that of the normally, i.e., without UST, implanted sample. This is sustained by the decreased yield of $[AgO]^{123}$ complexes in UST-implanted sample (shown on Fig. 3 with squares). Indeed, as the clusters become bigger, the contacting surface of Ag spheres with SiO_2 matrix decreases, leading to the $[AgO]^{123}$ yield reduction.

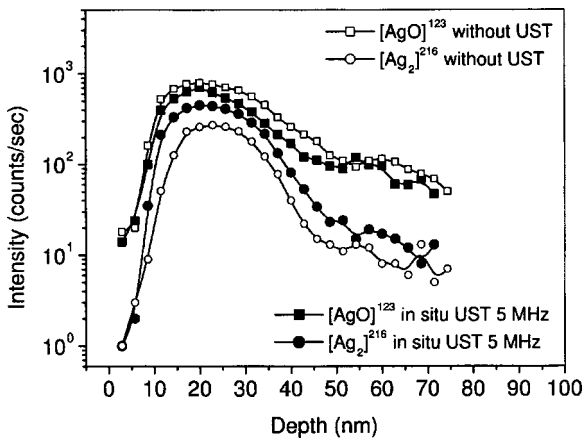

FIG. 3. ToF-SIMS profiles of $[Ag_2]^{216}$ (circles) and $[AgO]^{123}$ (squares) fragment ions in Ag-implanted SiO_2 at 3.0×10^{15} ions/cm^2, 40 keV, annealed in vacuum at 550 °C without UST (open symbols) and with *in situ* applied UST of 5 MHz (filled symbols).

IV. DISCUSSION

In order to understand the increment in cluster size upon the action of *in situ* applied acoustic waves, we consider the precipitation processes of silver in silicon oxide during postimplantation annealing. The precipitation process which leads to the formation of particles can be conditionally grouped into three different stages, each of them involving reactions with point defects: (i) nucleation, (ii) growth, and (iii) coarsening (also termed as Ostwald ripening). We treat now each stage separately and note that the degree to which each individual stage influences the enhanced cluster formation is not yet clear.

(i) The first stage is the homogeneous or heterogeneous formation of nuclei of the precipitating phase. In ion-implanted structures which possess high concentration of point defects acting as nucleation centers, the heterogeneous nucleation is most likely to take place. The critical radius of precipitate according to Vanhellemont and Claeys[15] is

$$r_c = 2\sigma \Big/ \frac{ExkT}{\Omega_p} \ln \frac{C_P}{C_P^*}\left(\frac{C_V}{C_V^*}\right)^{\beta}\left(\frac{C_I^*}{C_I}\right)^{\gamma} - 6\mu\delta\epsilon,$$

where C_P, C_V, and C_I are the precipitant, vacancy, and self-interstitial concentrations in the matrix, C_P^*, C_V^*, and C_I^* their thermal equilibrium values, γ the injected interstitials, β the absorbed vacancies, σ the SiO_2–Ag interface energy, Ω_p the molar volume of the Ag precipitate, kT the thermal energy, ϵ the constrained strain with $E=(1-\epsilon)^{-3}$, δ the linear misfit, μ the shear modulus of the lattice, and x the number of precipitating atoms per precipitate unit. Following this equation a supersaturation of self-interstitials will inhibit the growth of precipitates, while a supersaturation of vacancies decreases the value of r_c, i.e., stimulates growth. It has been shown[12] that crystal excitations by ultrasound enhance the diffusion of interstitials towards the bulk of the substrate and result in the accumulation of vacancies near the projected range region in boron-implanted silicon. A similar model is discussed in Ref. 16 where strain relaxation in helium-implanted SiGe layers is investigated. Therefore, the growth of Ag precipitates in structures implanted with the UST is enhanced as a result of a mechanical stress decrease and the presence of a large vacancy concentration.

(ii) The second stage is the diffusional growth of the clusters. The dominant mechanism for the diffusion of silver atoms in a SiO_2 host matrix is known to be vacancy-assisted diffusion where an atom that is attempting to move in a certain direction exchanges with a vacancy located at any of the nearest-neighbor sites.[17] Therefore, increased concentration of vacancies in US-treated samples enhances the diffusion of silver atoms, resulting in an increase in cluster diameter. Another possible diffusion mechanism is the ring diffusion in which the ring or cyclic exchange of neighboring atoms takes place. The required correlation of the atom motions within a ring rises rapidly as the number of participating atoms increases. For larger ring groupings it becomes highly unlikely that correlated cyclic ring exchange will occur.

(iii) The third stage is the coarsening stage, often denoted as Ostwald ripening. This growth stage is governed by the Gibbs-Thomson effect where the chemical potential of a cluster is inversely proportional to the cluster size. This means that in a system containing both large and small particles, the difference in chemical potential leads to material transfer from small to large clusters. Taking into account that Ostwald ripening is a diffusion-driven process whose kinetics is governed by the diffusion coefficient D, a demarcation between a diffusional growth and a coarsening process is somewhat arbitrary.

Hence, the increase of Ag cluster size in ion-implanted silica upon the action of ultrasound vibrations is related to the spatial separation of the point defects during ion implantation. The vacancy excess substantially increases the diffusion coefficient of silver atoms and precipitate growth rate, resulting in enhanced clustering processes.

V. CONCLUSIONS

The precipitation process of ion-implanted silver upon the action of *in situ* acoustic vibrations was investigated with TEM and ToF-SIMS. We have shown that *in situ* applied ultrasonic treatment leads to increased precipitate size after postimplantation annealing. The physical mechanism of this effect is attributed to the spatial redistribution of point defects and vacancy accumulation in the precipitation region.

ACKNOWLEDGMENT

We wish to thank Alan Savan (Center of Advanced European Studies and Research, Bonn, Germany) for careful reading of the manuscript.

[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).
[2] F. Gonella and P. Mazzoldi, *Handbook of Nanostructured Materials and Nanotechnology* (Academic, San Diego, 1989).
[3] R. F. Haglund, Jr., Mater. Sci. Eng., A **253**, 275 (1998).
[4] P. D. Townsend, P. J. Chandler, and L. Zhang, *Optical Effects of Ion Implantation* (Cambridge University, Cambridge, 1994).
[5] R. A. Zuhr, R. H. Magruder III, and T. S. Anderson, Surf. Coat. Technol. **103–104**, 401 (1998).
[6] D. Ila *et al.*, Nucl. Instrum. Methods Phys. Res. B **191**, 416 (2002).
[7] M. Dubiel, H. Hofmeister, G. L. Tan, K.-D. Schicke, and E. Wendler, Eur. Phys. J. D **24**, 361 (2003).
[8] A. L. Stepanov and V. N. Popok, Surf. Sci. **566–568**, 1250 (2004).
[9] J. Roiz, A. Oliver, E. Munoz, L. Rodriguez-Fernandez, J. M. Hernandez, and J. C. Cheang-Wong, J. Appl. Phys. **95**, 1783 (2004).
[10] V. N. Pavlovich, Phys. Status Solidi B **180**, 97 (1993).
[11] W. H. Franklin and T. Sengupta, IEEE J. Quantum Electron. **8**, 393 (1972).

[12]D. Krüger, B. Romanyuk, V. Melnik, Ya. Olikh, and R. Kurps, J. Vac. Sci. Technol. B **20**, 1448 (2002).
[13]S. Ostapenko, Appl. Phys. A: Mater. Sci. Process. **A69**, 225 (1999).
[14]B. El-Karah, *Fundamentals of Semiconductor Processing Technologies* (Kluwer, Dordrecht, 1995), p. 39.
[15]J. Vanhellemont and C. Claeys, J. Appl. Phys. **62**, 3960 (1987).
[16]B. Romanyuk *et al.*, Mater. Sci. Semicond. Process. **8**, 171 (2005).
[17]M. E. Glicksman, *Diffusion in Solids* (Wiley, New York, 2000), p. 224.