Note: This is a preprint of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the author(s).

To be submitted to 1993 Fall MRS Meeting, Boston, Mass.

Nanosize Metal Alloy Particle Formation in Ag and Cu Sequentially Implanted Silica

R. A. Zuhr
Oak Ridge National Laboratory
Oak Ridge, Tenn.

R. H. Magruder, III, T. A. Anderson, and J. E. Wittig
Vanderbilt University
Nashville, Tenn.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

December 1993

MASTER

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED

NANOSIZE METAL ALLOY PARTICLE FORMATION IN AG AND CU SEQUENTIALLY IMPLANTED SILICA

R. A. Zuhr, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
R. H. Magruder, III, T. A. Anderson and J. E. Wittig, Dept. of Applied and Engineering
Sciences, Vanderbilt University, Nashville, TN 37235

ABSTRACT:

A series of high purity silica samples were sequentially implanted with Ag and Cu ions at energies such that the depth distributions for each of the ions overlap. The samples were characterized by RBS, TEM and optical spectroscopy. The optical response was found to be dependent on the order of sequential implantation as well as the relative concentration of the implanted elements. The changes in the optical response are attributed to composition changes of the metal colloids that are formed as a result of alloying of the sequentially implanted metal ions, as well as to changes in the size the colloids.

INTRODUCTION:

Recently composites of nanosize metal particles (2-30 nm in diameter) embedded in glass have been shown to exhibit third order optical nonlinearities with a magnitude of 10^{-11} esu and a response time less than 5 ps.^{1,2} The large nonlinear susceptibility is attributed to local-field enhancement of the third-order nonlinear susceptibility $\chi^{(3)}$ for frequencies near the surface plasmon resonance of the metallic particles. In a recent series of papers, we^{2,3} have shown that the effective nonlinear response of a composite of nanosize Cu particles formed in silica by ion implantation is strongly enhanced near the surface plasmon resonance. Magruder et al⁴ have demonstrated that planar layers of Au nanosize particles formed in silica by implantation have an effective nonlinear susceptibility that is 200 times that of similar size Au clusters (5-30 nm in diameter) embedded in ruby gold filter glass. This enhancement was attributed to an increased volume fraction of the particles and to mutual interactions between the particles due to their close proximity.

As strong enhancements of the nonlinear response due to local field effects are expected to occur on or near the surface plasmon resonance of the metal particles, the ability to control the frequency of the surface plasmon resonance is of interest for possible wavelength tunability. In this paper we show how the frequency of the surface plasmon resonance can be modified with sequential implantation. The position and magnitude of the surface plasmon resonance depend on both the order of sequential implantation and the relative concentrations of the ions implanted.

EXPERIMENTAL PROCEDURE:

Four optical quality samples of Corning 7940, 20 mm in diameter and 1 mm thick, were implanted with singly charged Cu ions at an energy of 160 keV and a dose rate of 2.5 $\mu\text{amps}/\text{cm}^2$ to a nominal dose of 6×10^{16} ions/ cm^2 in each sample. These samples were then implanted with singly charged Ag ions at an energy of 300 keV and a dose rate of 2 $\mu\text{amps}/\text{cm}^2$ to nominal doses of 1, 2, 4 and 6×10^{16} ions/ cm^2 . A fifth sample was implanted first with 6×10^{16} ions/ cm^2 Ag at 300 keV and then sequentially implanted with 6×10^{16} ions/ cm^2 of Cu. The implantation energies were chosen using TRIM 89⁵ calculations to indicate energies where the depth distributions of the elements would overlap. This results in a planar thin film of sequentially implanted Cu and Ag ions whose depth of implantation is approximately the same. Ion backscattering with 2.3 MeV He⁺

ions at a scattering angle of 160° was used to measure the depth profile of the implanted metals for all samples.

Samples for transmission electron microscopy (TEM) were prepared by cutting 3 mm diameter discs from the implanted wafers with a slurry drill, mechanical grinding of the disc from the backside to a thickness of about 100 microns, and dimple grinding to approximately 20 microns from the implanted surface. Final thinning to electron transparency was achieved by planar backthinning by ion milling with a single Ar gun at 6 keV. To minimize ion damage, the samples were cryogenically cooled during ion milling. The samples were carbon coated to eliminate charging effects. Greater detail of sample preparation can be found in prior work.⁶ These samples were examined in a Philips CM20/T scanning transmission electron microscope operating at 200 keV. Standard bright field (BF) imaging and selected area electron diffraction were used to characterize the implanted layer of the silica wafers. The energy dispersive spectra were made using the scanning transmission electron microscope (STEM) mode. Area scans were made over a micron range and scans on single particles were made using a 20 nm diameter probe.

Optical measurements were made at room temperature in air from 650 to 200 nm (1.8 to 6.2 eV) using a Cary 5 dual beam spectrometer. All samples were measured using an unimplanted sample in the reference beam. Hence, all absorption measurements are reported as the difference between implanted and unimplanted glasses. The spectra are normalized to implanted dose, i.e. extinction coefficient. The absorption spectra are reported in this fashion to normalize differences in total dose between the different samples. The absorption spectra were measured at three different positions on each sample. The scatter in extinction coefficient due to these different positions is less than 3%.

RESULTS:

Rutherford Backscattering (RBS) measurements of the depth profiles of the implanted Cu and Ag are shown in Fig. 1 for nominal Ag doses of (a) 1×10^{16} /cm² and (b) 6×10^{16} /cm² at 300 keV on top of 6×10^{16} /cm² Cu at 160 keV. The results for these two doses are representative of the other doses used in this work, and show a large degree of overlap for the implanted elements, as predicted by the TRIM calculations. The overlap region, determined primarily by the narrower depth distribution of the Ag, is about 80 nm wide and is centered at a depth of about 125 nm. The bimodal distribution of the implanted copper is not predicted, but has been observed previously,⁷ and occurs even without the sequential implantation of Ag. However, as can be seen from the measured change in the Cu distributions for different Ag doses, there is clearly diffusion of the Cu atoms during the Ag implantation which could lead to agglomeration, alloying, and colloid formation even at room temperature.

Figure 1 RBS depth profiles of Ag and Cu implanted in silica at nominal Ag doses of (a) 1×10^{16} /cm² and (b) 6×10^{16} /cm² at 300 keV on top of 6×10^{16} /cm² Cu at 160 keV.

Figure 2 Plan view TEM micrographs of silica implanted at room temperature with 6×10^{16} Cu/cm² followed by (a) 2×10^{16} , (b) 4×10^{16} , and (c) 6×10^{16} Ag/cm².

Figures 2a,b,c show representative bright field (BF) images of the planar view of the implanted layer for the samples implanted with 6×10^{16} Cu ions/cm² and then sequentially with 2, 4 and 6×10^{16} Ag ions/cm² respectively. The nanosize particles formed are uniform in shape and are spherical. The mean particle sizes for the three samples are 3.7 ± 3.2 , 22.4 ± 6.0 , 27.6 ± 9.7 nm respectively for the three samples. The volume fraction of the Ag-Cu alloy metal particles is $\sim 5\%$ in the center of the implanted region. The particles are separated by distances comparable to the dimensions of the colloids. Selected area diffraction patterns from the samples reveal that two distinct metallic crystal structures exist in the implanted layer. In the sample implanted with 6×10^{16} Ag ions/cm² and 6×10^{16} Cu ions/cm², the predominant features in the polycrystalline ring patterns were representative of the face centered cubic (FCC) Ag lattice. However, a weaker set of rings consistent with FCC metallic Cu are also observed.

Energy dispersive X-ray spectra (EDS) from individual particles for the sample implanted with 6×10^{16} ions/cm² Ag and Cu indicate that the particles are made up of Ag rich and Cu rich alloys. Although quantitative chemical analysis is impaired due to the contributions from overlapping smaller particles to the EDS data, for a larger colloid

(~ 30 nm in diameter) in the sample implanted first with 6×10^{16} Ag ions and sequentially with 6×10^{16} Cu ions there is conclusive EDS evidence that the Ag rich particles contain a substantial amount of Cu ($20 \sim 40\%$), while the Cu rich particles contain $\sim 30\sim 40\%$ Ag. Similar analyses of the lower dose Ag sequentially implanted samples revealed that the particles formed do not share the same average ratio of Ag to Cu as the higher dose samples.

Figure 3 shows the extinction coefficient (EC) as a function of photon energy for the samples implanted with 6×10^{16} Cu ions/cm² and sequentially implanted with Ag. At the lowest Ag dose there are two peaks, one at ~ 3.2 eV and the second at ~ 2.2 eV. As the Ag dose increases the peak at 3.2 sharpens and moves to lower energy while the peak at 2.2 eV becomes at most a shoulder on the large peak. In figure 4 the EC is shown for the samples implanted with Cu and Ag and Ag then Cu. The sample implanted with Ag first has a peak at ~ 2.8 eV while the sample implanted with Cu first has a peak at ~ 3 eV.

DISCUSSION:

Depth profiles measured by RBS (Fig. 1) show that sequential implantations of Ag and Cu, at energies of 300 and 160 keV respectively, result in the formation of layers extending from 20 to 200 nm below the surface that contain significant amounts of each of the constituents and can thus contribute to the formation of alloyed colloidal particles. Cu in particular is mobile during room temperature ion irradiation by either self-ions, as demonstrated by the bimodal nature of the implanted Cu distribution, or by Ag ions, as shown by the change in the Cu distribution observed

Figure 3 Linear absorption spectra of silica implanted with Cu 6×10^{16} ions/cm² and sequentially implanted with Ag a) 6, b) 4, c) 2 and d) 1×10^{16} ions/cm²

Figure 4 Linear absorption spectra of silica implanted with Ag 6×10^{16} ions/cm² and sequentially implanted with Cu 6×10^{16} ions/cm²

during subsequent Ag implantation. Both Ag and Cu exhibit sufficient mobility during room temperature irradiation to form colloidal particles, so that both can contribute by diffusion to the formation of the alloy colloids observed in this work, regardless of the order of the sequential implantation.

The x-ray data clearly show that the particles formed, while varying somewhat in composition, are Ag-Cu alloy metal colloids. The composition ratio changes as the amount of implanted Ag is changed by sequential implantation in the first series of samples. There are two mechanisms responsible for absorption in the metal colloid-silica composites. The first source of absorption is defects created during ion implantation. The second is the presence of the nanosize particles and their interaction with the host substrate. Ion implantation is known to introduce defects such as the B₂, E'', peroxy and homobond centers in silica which have broad absorption bands at 5, 5.8, 7.5 and 7.6 eV respectively.^{8,9} Part of the linear absorption measured in the ultraviolet can be attributed to these defect centers.

The second absorption mechanism is the interaction of the metal particles with the incident radiation. We attribute the absorption in the range from 1.8 to 4.0 eV to the presence of the metal particles. For clusters with diameters less than $\lambda/20$, where λ is the wavelength of the incident radiation, the absorption is reasonably described by Mie scattering theory in the electric dipole approximation,^{10,12} and is given by

$$\alpha = \frac{18\pi n_d^3}{\lambda} \cdot \frac{p \cdot \epsilon_2}{[\epsilon_1 + 2n_d^2]^2 + \epsilon_2^2} \quad (1)$$

where α is the absorption, $\epsilon(\lambda) = \epsilon_1 + i \epsilon_2$ is the dielectric constant of the metal, p is the volume fraction of the metal particles and n_d is the index of refraction of the dielectric host. The absorption is expected to exhibit a peak at the surface plasmon resonance frequency where the condition $\epsilon_1 + 2n_d^2 = 0$ is met. The width of the absorption will also be determined by the dielectric function of the metal particle. The surface plasmon resonance frequency (or wavelength) depends on the detailed electronic properties of the metal clusters and on the index of refraction of the host dielectric, n_d . Assuming that n_d remains constant for the host dielectric, we will not consider it further and will instead focus on the contributions of the metal particles to the position of the surface plasmon resonance frequency.

The surface plasmon resonance (SPR) depends implicitly on particle size through the dielectric constant of the metal particles. The free-electron contribution will be modified if the mean free path of the electron in the particle is greater than the size of the particle.¹¹ With increasing particle size the resonance peak will increase in size and sharpen.¹² For particles with radii satisfying $r < \lambda/20$ only small shifts in the position of the surface plasmon resonance ($\sim 2-5\%$) are expected due to particle size.¹³ As our particles are sufficiently small to meet this criterion even for the highest dose samples, we do not expect shifts greater than $\sim 5\%$ in the position of the surface plasmon resonance frequency due to particle size effects.

The SPR peak is at ~ 2.2 eV for the single element Cu implanted silica and at 3.2 eV for the single element Ag implanted silica samples^{12,13}. The sequentially implanted samples exhibit significantly different optical spectra than the samples implanted with single elements. Shifts in both peak position and magnitude compared to the single implantations are observed. These results indicate that changes in the optical absorption are due to the presence of the two different metallic elements. The shift in the wavelength of the surface plasmon resonance with sequential implantation is attributed to the *alloying* of the Cu-Ag ions during implantation as observed in the dispersive x-ray analysis. The difference in optical response with increasing Ag concentration we attribute to different degrees of alloying and increasing particle size. The metal particles formed by sequential implantation will have different electronic structures depending upon composition, that will result in changes in the effective dielectric function of the particles. The position of the surface plasmon resonance is dependent on both the relative elemental concentrations of the sequentially implanted species and on the order of implantation. We attribute the change with relative elemental concentration to differences in the dielectric properties of the particles created. The surface plasmon frequency depends explicitly on the dielectric properties of the metal particles. Changes in the electronic structure of the particles due to alloying are expected to change the dielectric properties¹³ and hence the surface plasmon resonance frequency.

We attribute the changes in the amplitude and width of the surface plasmon resonance of the sequentially implanted samples, as compared to the single element samples, to differences in the composition of the particles as the amount of implanted Ag is varied, and to increasing particle size with increasing Ag concentration. From equation 2, at the surface plasmon resonance, the extinction coefficient, K , will be inversely related to the imaginary part of the dielectric function of the metal ϵ_2 by

$$K \approx C \frac{n_d^3 p}{\lambda \epsilon_2} \quad (2)$$

where C is a constant. The component of the dielectric function, ϵ_2 , has been given by Bohren and Huffman¹¹ as

$$\epsilon_2 = \epsilon_{2\text{-bulk}} + \frac{3\omega_p^2 v_F}{4\omega^2 a} \quad (3)$$

where v_F is the Fermi velocity of the electrons, ω_p is the plasma frequency, and a is the radius of the particle in angstroms. The nature of the optical response near the surface plasmon resonance is then affected by a change in the electronic properties of the colloid or by a change in the size of the colloid.

The changes observed with the order of implantation we attribute to changes in composition due to differences in the dynamics of particle formation. The dynamics of particle formation are different for single element implantations of Ag and Cu in silica. As the diffusion rates of Ag and Cu are different in silica, it is not unreasonable to expect the final composition to depend on the order of implantation.

CONCLUSIONS:

Based on the behavior of the single element particles in this and other work,^{2-5,12,13} and on the observations that the sizes, shapes, and volume fractions of the alloy particles are similar to those of single element particles, we attribute the frequency shift of the surface plasmon resonance frequency primarily to changes in the dielectric properties of the colloids as a function of particle composition. The observed changes in the magnitude of the optical response are attributed to changes in both the composition and the size of the particles that are formed under different implantation conditions.

ACKNOWLEDGMENTS:

The authors acknowledge the support of the Army Research Office under grant #DAAL03-91-G-0028 and Division of Materials Science, U.S. Department of Energy under contract DI-AC05-84OR21400 with Martin-Marietta Energy Systems, Inc.

-
1. D. Ricard, P. Roussignol and C. Flytzanis, *Opt. Lett.* **10**, 511 (1985).
 2. R. F. Haglund, L. Yang, R. H. Magruder, III, K. Becker, J. E. Wittig and R. A. Zuhr, *Opt. Lett.* **18**, 373 (1993).
 3. R. H. Magruder, III, R. F. Haglund, L. Yang, J. E. Wittig and R. A. Zuhr *MRS Proceedings, Optical Waveguide Materials*, Vol. **244**, 369 (1992).
 4. R. H. Magruder, III, L. Yang, R. F. Haglund, C. W. White, Lina Yang, R. Dorsinville and R. Alfano, *Applied Physics Lett.* **62**, 1730 (1993).
 5. J. Biersack and L. G. Haggmark, *Nucl. Inst. and Meth* **174**, 257 (1980).
 6. R. H. Magruder, III, D. L. Kinser, J. E. Wittig and R. A. Zuhr, *SPIE Proceedings*, vol. **1761**, 180 (1992).
 7. H. Hosano, H. Fukishima, Y. Abe, R. A. Weeks, and R. A. Zuhr, *J. Non-Cryst. Solids* **143**, 157 (1992).
 8. G. W. Arnold and P. Mazzoldi, *Ion Beam Modification of Insulators*, P. Mazzoldi and G. W. Arnold, eds. Elsevier, Amsterdam (1987).
 9. R. A. Weeks, *Materials Science and Technology Vol. 9*, J. Zarzycki, ed. VCH, Weinheim (1991).
 10. G. Mie, *Ann. Phys.* **25**, 377 (1908).
 11. C.F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley and Sons, New York (1983).
 12. U. Kreibig and L. Genzel, *Surf. Sci.* **156**, 678 (1985).
 13. R. E. Hummel, *Electronic Properties of Materials*, 2nd Ed., Springer - Verlag, Berlin (1993).

END

DATE

FILMED

317/94