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Au Colloids Formed by Ion Implantation in Muscovite Mica Studied by Vibrational and Electronic Spectroscopes and Atomic Force Microscopy

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Abstract

Au was implanted into the (001) surface of Muscovite mica at an energy of 1.1 MeV and at doses of 1, 3, 6, and $10x10^{16}$ ions/cm^2. Optical spectra of the as-implanted samples revealed a peak at 2.28 eV (545 nm) which is attributed to the surface plasmon absorption of Au colloids. The infrared reflectance measurements show a decreasing reflectivity with increasing ion dose in the Si-O stretching region (900-1200 cm-l). A new peak observed at 967 cm^{-1} increases with the ion dose and is assigned to an Si-O dangling bond. Atomic force microscopy images of freshly cleaved samples implanted with 6 and $10x10^{16}$ ions/cm^2 indicated metal colloids with diameters between 0.9- 1.5 nm. AFM images of the annealed samples showed irregularly shaped structures with a topology that results from the fusion of smaller colloids.

1. Introduction

The reduction of matter to the nanometer scale often leads to a manifestation of properties which differ significantly from the bulk. The thermodynamic, linear and nonlinear optical, structural, and mechanical are examples of properties which are modified when a materials is reduced to a finite dimension. Ultrafine scale gold particles have drawn much interest due to appearance of the surface plasmon polarition which is observed when the particle is reduced to the nanometer scale. [1] More recently gold nano-particles have shown to possess a large nonlinear optical response and have properties that are desirable for an all optical switching device .[2]

Several approaches have been taken to fabricate metallic nano-particles which include hydrosols, impregnation/chemical reduction, inert gas evaporation, vacuum evaporation, vacuum evaporation and matrix isolation, cluster beams, reverse micelles, and pressure impregnation.[3] We have taken the approach of using ion implantation into the (001) surface of mica to form colloids. The use of mica as a substrate has the advantage that it is atomically flat which allows for AFM measurements to be carried out to determine the colloid size in the as-implanted state and to follow the effects of annealing on colloid growth and aggregation. In addition, mica is reasonably transparent in the visible region and therefore, as a substrate, its permits the study of the surface plasmon resonance of Au nano-particles.

2. Experimental

Au implantation into (001) oriented mica at room temperature was carried out at energies of 1.1 MeV and at doses of 1, 3, 6, $10x10^{16}$ ions/cm^2. Thermal annealing was carried out at

temperatures between 200 and 5000 C in a reducing atmosphere (5% H_2 + Ar) with a one zone tube furnace.

The electronic spectra were measured between6.2-1.24 eV (200-1000 nm) with a Hitachi model 3501 UV-Vis-NIR spectrophotometer. A piece of virgin mica of the same thickness as the implanted sample was placed in the reference beam for normalization of the spectra. The resolution of the measurements near 550 nm was 0.2 nm. Repeated measurements showed the photometric accuracy to be $\pm$0.3 % transmittance and $\pm$0.2 nm in wavelength accuracy. The band centers were located from the extrema in second order derivative spectra.

The infrared reflectance spectra were obtained with aBomem MB- 100 Fourier transform spectrometer to cover the 4000-400 cm-l range. The samples were mounted on a laboratory built reflectance stage with a fixed angle of incidence of 150 .Typically, 200 interferograms were collected. The wavelength and photometric accuracy were 0.5 cm^{-1} and 0.4 % reflectance, respectively. All spectra were divided by a reference spectrum of a gold mirror. The band centers were obtained from extrema in the second derivative spectra.

All AFM images were recorded in the tapping mode with a Nanoscope III atomic force microscope from Digital Instruments. The height resolution reported for all measurements is $\pm$ 0.1 nm. Samples were prepared for AFM measurements by applying adhesive tape to the implanted surface and stripping away layers of mica. Both the mica adhering to the tape and that which remained on the implanted substrate were examined by electronic spectroscopy to identify where the colloids were located by the appearance of the surface plasmon polariton.

3. **Results**

The infrared reflectance spectra for mica implanted with Au at doses of 1, 3, 6, and $10x10^{16}$ ions/cm^2 are shown in figure 1 together with the reflectance spectrum of virgin mica. The spectrum for virgin mica shows two intense reflectance maxima located at 1096 and 1041 cm^{-1} and an unresolved shoulder at 1014 cm^{-1} and a weak peak at 904 cm^{-1}. The Au-implanted substrates show a decrease in reflectivity with an increase in ion dose. The corresponding bands in the ion implanted samples are redshifted from those of the virgin mica; the 1096 cm^{-1} peak shifts by 21 cm^{-1} to 1075 cm^{-1} and, the 1041 cm^{-1} peak shifts by 16 cm^{-1} to 1.025 cm^{-1} for the implanted samples. There is an appearance of a new peak at 967 cm^{-1} that is initially poorly resolved for the lowest ion dose, but it becomes more intense and better resolved as the ion

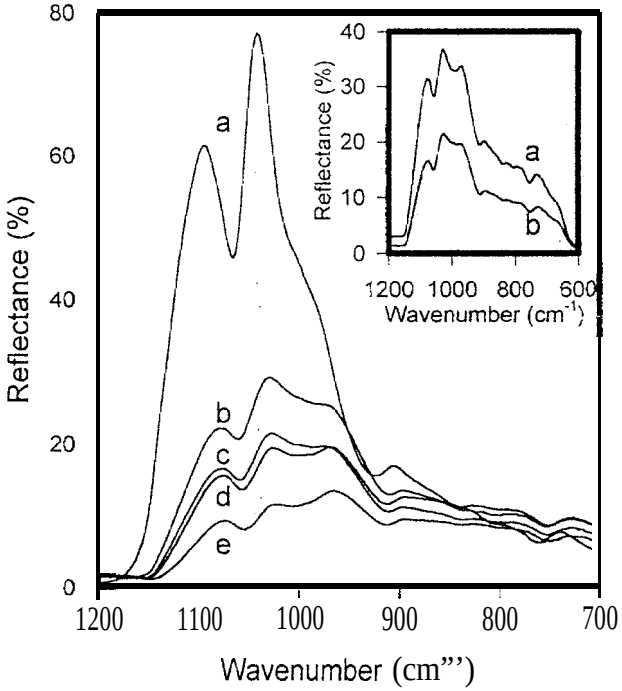


Figure 1. Infrared reflectance spectra for Au implanted: a) virgin, b)1e16, c)3e16, d)6e16 and 10e16 ions/cm^2. Inset 6e16 as-implanted and annealed at 500°C in 5 % H_2 +95% Ar.

dose increases. The 1014 cm-l feature observed in the virgin mica cannot be observed in the implanted samples because it is masked by the dominant intensity of the 967 cm^{-1} band.

The affect of annealing on the infrared spectra of the implanted samples is illustrated in the inset of figure 1. There is a significant increase in the reflectivity of for the annealed sample but, the peak at 967 cm^{-1} remains.

The electronic spectra are shown figure 2 for the mica substrates implanted with 1, 3, 6 and $10x10^6$ ions/cm^2. The prominent feature in the spectra appears at 2.28 eV (545 nm) and increases with the ion dose, There is a dose dependent increase in absorption at energies greater than 3 eV and virtually no absorption is observed for energies less than 1.2 eV. Annealing the samples at 5000 C results in an increased absorption at 2.28 eV and this is shown for the sample implanted $6x10^{16}$ ions/cm^2 in the inset of figure 2.

An AFM image of a freshly cleaved unannealed mica surface implanted with $10x10^{16}$ ions is shown in figure 3. The areas of high contrast appearing as white spikes correspond to heights between 1.03-0.59 nm and are attributed to Au colloids. Further analysis of the data indicates that 86% of the colloids are 0.88 nm in diameter, while 8% are 0.59 nm and the remaining 6% are 1.03 nm in diameter.

The results of a sample annealed at 500°C for 1 hour are shown in figure 3. The main feature observed in the image is the area of white contrast which shows an irregular shaped feature -1 nm in height, The image shows domains that suggest that irregular shaped feature is composed of smaller clusters that have begun to fuse together during the annealing.

Figure 4 shows an image of an annealed sample implanted with $10x10^{17}$ ions/cm^2 where two (001) planes are separated by several steps (40 rim). It is clear from the image that colloids on the two planes differ significantly in size.

4. Discussion

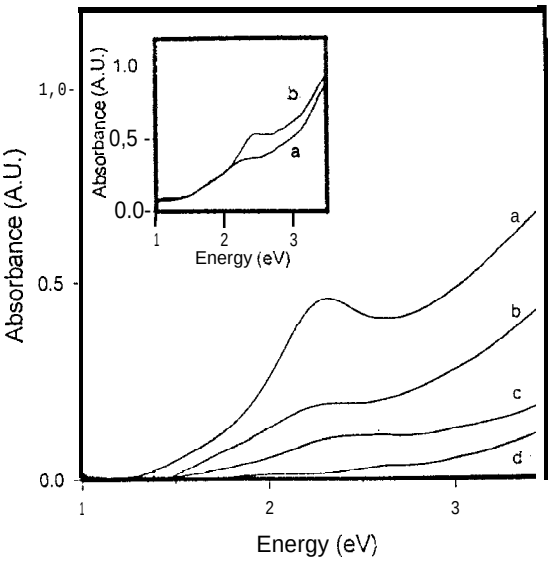
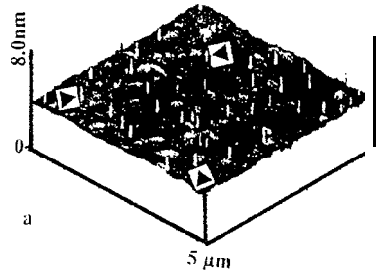


Figure 2. Electronic spectra for Au implanted in mica at 10e16, 6e16, 3e16 and 1e16 ions/cm^2 from top to bottom. Inset shows the effect of annealing the same sample under the same conditions as shown the inset of figure 1.



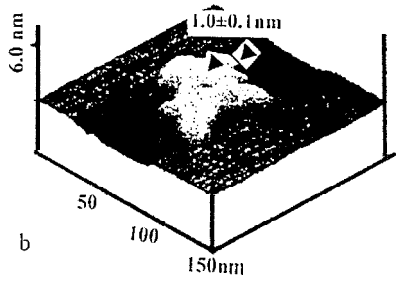


Fig 3. a) An AFM image of Au implanted in mica (10e17). The same sample annealed at 500° in 5 % H_2 + 95% Ar. Arrows indicate height of the cluster above the (001) plane.

The peaks observed for the virgin mica in the infrared spectra between 900-1200 cm-l can be attributed to Si-O stretching vibrations.[4] The decrease the frequencies and intensities of the Si-O stretching vibrations which occurs with the concomitant appearance of the peak at 967 cm-* is attributed to a decrease in the number of oscillators that absorb in 1100- 1200 cm" [1] region. The decrease in the number of Si-O oscillators is in turn attributed to the ion induced rupture of the Si-O-Si bridge bonds. The red shift in the Si-O stretching vibrations is due to a decrease in the force constant associated with the Si-O stretching vibration and also to changes in the G-matrix elements in the Wilson secular equation. [5] The peak observed at 967 cm-l in the Au-implanted mica sample correlates reasonably well with the frequency assigned to the Si-O dangling bond vibration for fused silica implanted with heavy ions.[6] On this basis we attribute the peak at 967 cm^{-1} in Au implanted mica to a Si-O dangling bond defect. Annealing the samples restores some of the intensity to the Si-O stretching region, but the persistence of the peak at 967 cm^{-1} indicates that the extensive defects remain in the lattice.

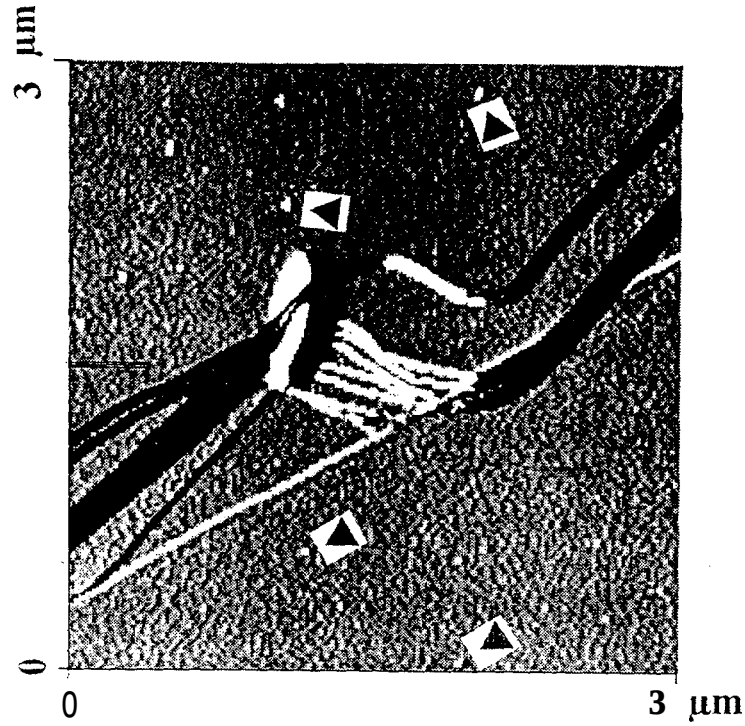


Fig 4. An AFM imageof mica implanted with 1e17 ions/cm^2. The arrows point to colloids to colloids separated on different planes that are separated by 40 nm.

The most significant feature in the electronic spectra is the peak at 2.28 eV which grow on annealing. By comparison to other studies Au implanted into sapphire and fused silica where the surface plasmon polarition is observed at 2.25 eV,[7] we assign the 2.28 peak in mica to the surface plasmon polariton to Au colloid in mica.

Figure 4 shows the Au colloids on two (001) planes of mica separated by 40 nm. The data are presented with z-axis in terms of deflection for clarity. It is clear from the image that the colloids on the upper plane are much larger than those in the lower plane. The difference in the sizes of the colloids must be due to that fact that the implanted profile has a Gaussian distribution. Thus, the colloids on the lower plane must be closer to the surface than those on the upper plane.

5. **Conclusion**

Au colloids have been fabricated by ion implantation into the (001) surface of mica. The surface plasmon polariton was observed at 2.28 eV. A band at 967 cm^{-1} was attributed to a Si-O dangling bond defect. The size of the colloid on different (001) planes is correlated with the Gaussian implantation profile. The use of mica as a substrate for metal colloid fabrication, and for the synthesis of quantum dots by sequential ion implantation[8] when combined with AFM may open new avenues for manipulating nanostructures on an atomically flat, insulating surface.

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References

1. R. J. Warmack and S. L. Humphrey, Phys. Rev. 334,2246 (1986).
2. K. Fukumi, A. Chayahara, K. Kodono, T. Sakaguchi, Y. Horino, M. Miya, K. Fujii, J. Hayakawa, and M. Satou, J. Appl. Phys. 75, 3075 (1994).
3. W. P. Halperin, Rev. Mod. Phys. 58, 533 (1985).
4. D. O. Henderson, M. A. George, Y. S. Tung, A. Burger, S. H. Morgan, W. E. Collins, C. W. White, R. A. Zuhr, and R. H. Magruder, J. Vat. Sci. Technol. A13, 1254 (1995).
5. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, The Theory of Infrared and Raman Vibrational Spectra, (Dover Publications, New York 1980) p.65.
6. R. H. Magruder, D. O. Henderson, and R. A. Zuhr, J. Non-Cryst. Solids 152, 258 (1993).
7. D. O. Henderson, R. Mu, Y. S. Tung, M. A. George, A. Burger, S. H. Morgan, C. W. White, R. A. Zuhr, and R. H. Magruder, J. Vat. Sci. Technol. B13, 1198 (1995).
8. C. W. White, J. D. Budai, J. G. Zhu, S. P. Withrow, R. A. Zuhr, Y. Chen, D. M. Hembree, R. H. Magruder, and D. O. Henderson, accepted for publication in the Fall 1994 Materials Research Society Meeting Symposium F: Microcrystalline and and Nanocrystalline Semiconductors, ed. by L. Brus, R. W, Collins, M. Hirose, and G. Koch.