Interaction between clusters in ion implanted and ion beam mixed SiO$_2$:Ag films

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Abstract

Spectra of optical extinction in the visible range for SiO$_2$:Ag colloid films prepared by ion implantation and ion beam mixing are compared to calculations for isolated clusters and for interacting clusters in an effective medium. Whereas for low metal concentrations the shape of the spectra is determined by the cluster size, at higher concentrations it largely depends on their mutual interaction. This interaction induces a broadening of the resonance in implanted films and on the contrary a narrowing in ion beam mixed films. The difference is ascribed to a particular arrangement of the clusters, with a bimodal size distribution, in the latter films. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Noble metals have been implanted in insulators for 20 years with the purpose of obtaining colloids with a high filling factor close to the surface, expecting that they exhibit a stronger non-linearity of refractive index than other deposits treated thermochimically [1]. One must however acknowledge that the cost of such implantations and the inhomogeneity in size and depth distribution of the metal clusters limit the potentialities of applications. More recently it has been proposed to use instead ion beam mixing of oxide/metal/oxide superimposed layers to achieve the same purpose, with ion fluences an order of magnitude lower. The result of irradiation is, stricktly speaking, not a real mixing in these systems, due to the insolubility of noble metals in most of the oxides considered (SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$) [2]. A lateral diffusion of the metal atoms to form spheroidal particles of sizes 2–3 times the metal layer thickness is observed instead. In addition, Rutherford backscattering spectra and TEM images recorded after irradiation with increasing ion fluences (Φ) have shown that the metal atoms ejected from these large particles by collisions can diffuse over significant distances with respect to the cascade dimension before precipitating again. The new clusters of sizes around 1 nm formed by this mixing–unmixing
process (hereafter labelled nano-clusters) are arranged in a concentric halo around the central particles (labelled macro-clusters) and their number increases in proportion to \( U \) as the number of displaced atoms \([2,3]\). It will be shown that the optical absorption peak in the visible range of these colloid films with bimodal distribution of cluster sizes is much narrower than that of implantation films containing a comparable volume fraction of metallic phase, due to this particular arrangement.

The Mie theory \([4]\) allows to calculate the exact optical response of the system by solving the Maxwell equations in the medium, provided that the clusters are spherical and isolated from each other. But the filling factor of clusters is generally high in ion implanted or ion beam mixed films since it is the purpose of using these techniques. In this case, it is necessary to use an effective medium theory, not so exact as the Mie theory but permitting to take into account the shape of clusters and their interaction, depending on their spatial arrangement and filling factor \([5]\). The purpose of this paper is to demonstrate, on the basis of such calculations, that it is essential to take into account these factors for interpreting the optical response of implantation or ion beam mixed layers.

2. Experiments

The conditions of films deposition and ion beam irradiation are detailed in references \([2,3]\). Implantations of \(10^{16}, 2 \times 10^{16}, 5 \times 10^{16} \) and \(10^{17} \) ions/cm\(^2\) were performed in silica (Herasil grade) at an energy of 150 keV. RBS analyses of these samples account for a Gaussian distribution of Ag concentration peaking at 76 nm and with a width of 19 nm for the fluences of 1 to \(5 \times 10^{16}\) (concentrations of 3\%, 6\%, 15\%), in agreement with TRIM calculations. No significant sputtering occurs for the highest fluence but the Ag concentration, of 28\%, is more homogeneous in the outer 40 nm.

Samples for ion beam mixing experiments were prepared by successive electron-gun evaporation of Ag and SiO\(_2\) layers under a residual pressure of \(10^{-5}\) Pa and irradiated with incremented fluences of 4.5 MeV Au ions. We preferred to study single metal layers, buried beneath 100 nm SiO\(_2\), and not multilayers with a more homogeneous depth distribution of clusters, because this enabled us to correlate the modifications of optical transmittance with the known mixing kinetics in this type of specimens \([2]\). The dependency of the strength of the resonance on the initial layer thickness will be discussed in a more detailed paper. Spectra of a 8 nm mixed layer have been chosen here as an example.

Plane-view and cross-sectional TEM imaging was used to study the variation of size and density of clusters in the two types of films as a function of the ion fluence \( U \). Measurements of optical extinction were made from 200 to 800 nm using a Cary UV–VIS–NIR dual beam spectrometer.

3. Results and discussion

3.1. Comparison to simulations for isolated clusters based on Mie theory

The principles of calculating absorption, scattering and extinction cross-sections \( \sigma \) of plasmon polaritons in isolated clusters, based on the Mie theory, are given in detail in \([4]\).

For irradiations with 4.5 MeV Au ions at fluences above \(5 \times 10^{15}\) ions/cm\(^2\), well separated and rounded macro-clusters surrounded by a halo of nano-clusters are observed by TEM in ion beam mixed layers (Fig. 1). Macro-clusters have a mean radius \( R \) of 2.5 times the layer thickness. The optical extinction spectra of SiO\(_2\)/Ag/SiO\(_2\) superimposed layers irradiated with lower fluences will not be analysed in this paper because their complex shape is due to a great extent to the incomplete transformation of the Ag layer into spherical balls. For fluences above \(5 \times 10^{15}\) the mean energy of the extinction peak shows no changes but the peak height increases and its width decreases with increasing number of nano-clusters \([3]\). The resonance in a specimen irradiated with \(1.6 \times 10^{16}\) ions has been compared to a sum of simulations for isolated clusters, applying the experimental size distribution determined by TEM (Fig. 2). The height of the sum has been normalized to that of
the experimental peak (also applied to all simulations in this paper). The simulated resonance is much narrower than the experimental peak and is centred at lower energy. Clusters of sizes 1–5 nm in the histogram of Fig. 1 (larger range than the actual range of nano-clusters sizes of 1–2 nm) contribute for less than 5% to the area of the calculated peak, because of the variation of the extinction cross-section $\sigma_{\text{ext}}$ in proportion to $R^3$ [4]. A better fit of the same experimental peak is however obtained with a normalized simulation for clusters with a uniform size $R$ of 2.85 nm. This remark may illustrate how unrealistic cluster sizes can be deduced from resonance peak analysis only, without control by TEM observation.

A wide distribution of cluster sizes is observed by TEM in silica implanted with $10^{17}$ Ag/cm$^2$ (Fig. 3). The percentage of clusters decreases monotonically with their increasing size, ranging from 2 to 20 nm. For comparing to Mie simulations the appropriate
way to average the size consists in weighting the number of clusters by their volume, since \( \sigma_{\text{ext}} \) of a cluster varies as \( R^3 \). The average radius found for this fluence is of 9 nm. The size of clusters formed for the fluence of \( 10^{16} \) Ag/cm\(^2\) is more homogeneous and of 1.4 nm. Mean sizes for the two others fluences should be of the order of 2–3 and 4–5 nm.

The extinction peak from these films becomes wider, asymmetric and the position of the resonance maximum shifts from 3.1 to 2.5 eV with increasing Ag concentration (Fig. 4). The peak recorded for the fluence of \( 10^{16} \) Ag ions/cm\(^2\) is relatively well fitted up to the interband absorption edge (about 3.8 eV), using Mie calculations with a...
radius of 1.0 nm. For the fluence of $2 \times 10^{16}$ Ag ions/cm$^2$, the width of the peak is closer to that predicted by the Mie theory for clusters with a uniform size of 1.35 nm than for a size in the range 2–3 nm. Mie resonances for clusters of any size in the range 5–20 nm are centred at a constant energy of 3.1 eV and their width decreases from 0.20 to 0.12 eV with the increasing radius. The strong broadening and shift of the resonances recorded for Ag fluences of $5 \times 10^{16}$ and $10^{17}$ cm$^{-2}$ with respect to Mie calculations for the mean sizes (or the size distribution determined by TEM for the fluence of $10^{17}$ Ag) must be ascribed to a strong effect of polarization by neighbors.

### 3.2. Comparison to simulations for interacting clusters

The validity of effective medium models is limited to the “quasi-static” regime where clusters behave as dipoles [4]. According to Mie calculations, the contribution of multipoles of higher order to absorption and scattering can be neglected for clusters of radius $R \leq 40$ nm in the case of Ag. In the effective medium model presently used [5], the fundamental expression of electrodynamics for the polarizability $\alpha$ of the metal clusters is modified by introducing in the latter a parameter $\beta$ accounting for the dependence of $\alpha$ on the shape of the clusters. The model uses the Lorentz formalism to estimate the electric local field at a cluster position by separating the contribution of close and remote clusters. The ratio of the contribution of close clusters (which may largely vary depending on the spatial distribution) to that of remote clusters is quantified by means of a parameter $K$. Increasing the filling factor $f$ in calculations based on this model results in a red shift of the resonance peak and the appearance of a tail on its high energy side when $f$ reaches 10%. With respect to simulations with a realistic value of $f$ (30%), for spherical clusters ($\beta = 1/3$) without effect of the local arrangement on their polarization ($K = 0$), the resonance peak recorded for the SiO$_2$ sample implanted with $10^{17}$ Ag ions (Fig. 4) is much broader and those of the SiO$_2$/Ag 8 nm/SiO$_2$ mixed layers are shifted to high energy by $+0.1$ eV. Since the clusters observed in TEM exhibit spherical shape, the broadening of experimental resonances in implantation films must be ascribed to fluctuations of the local arrangement and the shift in ion beam mixed specimens to a mean value of $K$ differing from zero. Simulations have been performed with distributions of factor $K$. The fluctuations of the $K$ factor are probably already noticeable in the sample implanted with $2 \times 10^{16}$ Ag because the apparent mean size does not change when taking into account the filling factor of 6% in the calculation. In the case of SiO$_2$ samples implanted with $5 \times 10^{16}$ and $10^{17}$ Ag ions the found distributions of $K$ are comparable and centred at a positive value, which means that clusters on average increase the polarization of their neighbors (Fig. 4). On the contrary, the mean value of $K$ in ion beam mixed samples is negative and the distribution becomes narrower with increasing ion fluence (Fig. 2). Our interpretation of this effect is that nano-clusters arranged in a spherical halo around each macro-cluster act on the local electric field as charges uniformly distributed at the surface of a sphere (depolarization field $E = -4\pi/3|\sigma|$).

### 4. Conclusion

A careful examination of the size distribution and of the spatial arrangement of clusters by means of TEM is necessary for interpreting optical properties of metal:insulator colloids. When the clusters are scattered at random and their filling factor lower than 5% like in silica implanted with low Ag fluences, calculations based on Mie theory can be used for finding the mean size of the clusters. This is useful since this size is hardly measurable on TEM images. Clusters formed by ion implantation of 6–30% Ag or ion beam mixing of layers with thickness up to 15 nm are not too big for neglecting the contribution of quadrupole absorption and scattering. But the filling factor and the local arrangement (factor $K$) of the clusters affect the resonance damping. In implantation layers this damping increases with the Ag concentration due to the increase of both size distribution and distance fluctuations between clusters. On the contrary, the macro-clusters formed by lateral segregation in sandwich layers appear more and more isolated under irradiation because their
mutual interaction is screened by the precipitation of a spherical halo of nano-clusters.

References


