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Penninkhof, J. J.; Polman, A.; Sweatlock, L. A.; Maier, S. A.; Atwater, H. A.; Vredenberg, A. M.; Kooi, B. J.

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Mega-electron-volt ion beam induced anisotropic plasmon resonance of silver nanocrystals in glass

J. J. Penninkhof[a] and A. Polman
FOM Institute for Atomic and Molecular Physics (AMOLF), Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Luke A. Sweatlock, Stefan A. Maier, and Harry A. Atwater
Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125

A. M. Vredenberg
Department of Atomic and Interface Physics, Debye Institute, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands

B. J. Kooi
Department of Applied Physics, Materials Science Center, University of Groningen, Nijenborgh 4, 4797 AG Groningen, The Netherlands

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30 MeV Si ion beam irradiation of silica glass containing Ag nanocrystals causes alignment of Ag nanocrystals in arrays along the ion tracks. Optical transmission measurements show a large splitting of the surface plasmon resonance bands for polarizations longitudinal and transversal to the arrays. The splitting is in qualitative agreement with a model for near-field electromagnetic plasmon coupling within the arrays. Resonance shifts as large as 1.5 eV are observed, well into the near-infrared. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1627936]

The interaction of light with small metal clusters embedded in a dielectric medium has been investigated extensively for many years.[1] Nanometer-sized clusters of noble metals in glasses exhibit strong absorption of visible light, due to collective motions of the free electrons which are called surface plasmons. The resonance frequency in spherical, noninteracting clusters depends on the size and the dielectric constants of the metal and the surrounding medium. In ensembles of particles, electromagnetic coupling among particles causes plasmon bands to shift.[2] Numerical simulations showed the effect of particle size, next-neighbor distance, number of particles and shape of aggregates on the extinction spectra of aggregates of nanometer-sized silver spheres.[3] Significant plasmon blue- and redshifts are predicted for strongly coupled ensembles. Very recently, it was shown experimentally that such interacting metal nanoparticles can serve as miniature waveguides in which electromagnetic energy can be transported via a dipolar near-field interaction.[4]

It is thus clear that nanoscale arrangements of metallic particles in glass are of great interest to study the fundamentals of plasmon interactions on small length scales. By tuning the interparticle interaction and particle shape, the plasmon resonance can be shifted to a wavelength of 1.5 μm. This may enable several applications in telecommunication, including polarization-dependent waveguides and nonlinear optical devices which take advantage of the high electromagnetic fields in plasmonic structures.

Recently, we have shown that anisotropic metal colloids can be fabricated controllably by mega-electron-volt (MeV) ion irradiation of colloidal particles which consist of a gold core surrounded by a silica shell.[5] This shape change is attributed to an anisotropic deformation effect in the silica that is known to occur in amorphous materials.[6] In this letter, we describe the effect of MeV ion irradiation on silver nanocrystals embedded in a planar sodalime glass film. Optical transmission data show polarization-dependent plasmon bands of silver, with red and blue plasmon shifts occurring for polarizations parallel and orthogonal to the irradiation axis, respectively. The splitting is attributed to an ion beam induced alignment of the Ag nanocrystals into linear arrays and can be tuned by varying the ion fluence.

Silver nanocrystals were made in a sodium-containing borosilicate glass by a combination of $Na^+ \leftrightarrow Ag^+$ ion exchange and ion irradiation.[7] A 1-mm-thick Schott BK7 glass wafer was immersed in a salt melt containing 5 mol % $AgNO_3$ in $NaNO_3$. One sample was ion exchanged for 7 min at 310 °C, other samples for 10 min at 350 °C. After the ion exchange, Ag nanocrystals were nucleated by a 1 MeV Xe irradiation (normal incidence, room temperature, $1 \times 10^{16}/\mathrm{cm}^2$). This nanocrystal formation process is well-documented and ascribed to the enhanced mobility of Ag ions due to atomic displacements caused by the ion beam.[7,8] Subsequently, the samples were subjected to a 30 MeV Si ion beam at 77 K under an angle of 60° off-normal. Si ions at this high energy exhibit very high electronic energy loss, a prerequisite for anisotropic deformation processes which are thought to be caused by the highly anisotropic thermal spike along the ion trajectory. The Si beam flux was in the range of $(1-5) \times 10^{11}/\mathrm{cm}^2\,\mathrm{s}$. Fluences were chosen between 0 and $3 \times 10^{15}/\mathrm{cm}^2$. Note that the fluences projected normal to the surface are half these values.

Rutherford backscattering spectrometry was performed to determine the composition of the glass after the ion ex-

[a]Electronic mail: penninkhof@amolf.nl; URL: http://www.amolf.nl

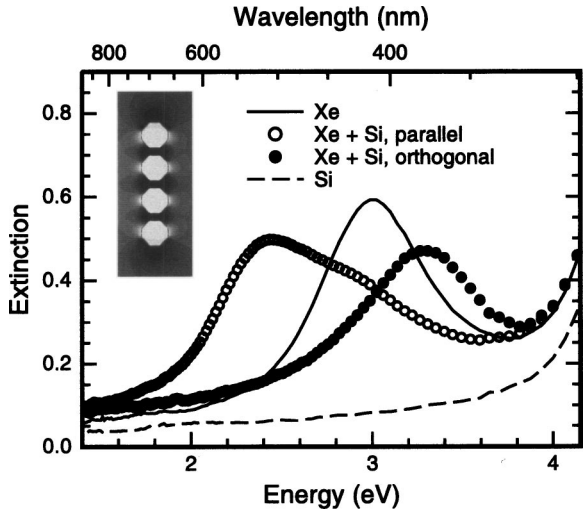

FIG. 1. Optical extinction spectra of Ag ion exchanged BK7 glass samples irradiated with 1 MeV Xe (drawn line) to form Ag nanocrystals, and with subsequent 30 MeV Si under an angle of 60° off-normal (circles), using normal-incidence light. The Si irradiation ($2\times10^{14}/\mathrm{cm}^2$) causes a large split in the plasmon bands for polarizations transverse (closed circles) and longitudinal (open) to the direction of the Si beam as projected onto the surface. The inset shows a representative time snapshot of the electric field amplitude distribution obtained from a FDTD simulation with enhanced field amplitudes both inside (white, positive field) and between (black, negative field) the Ag particles.

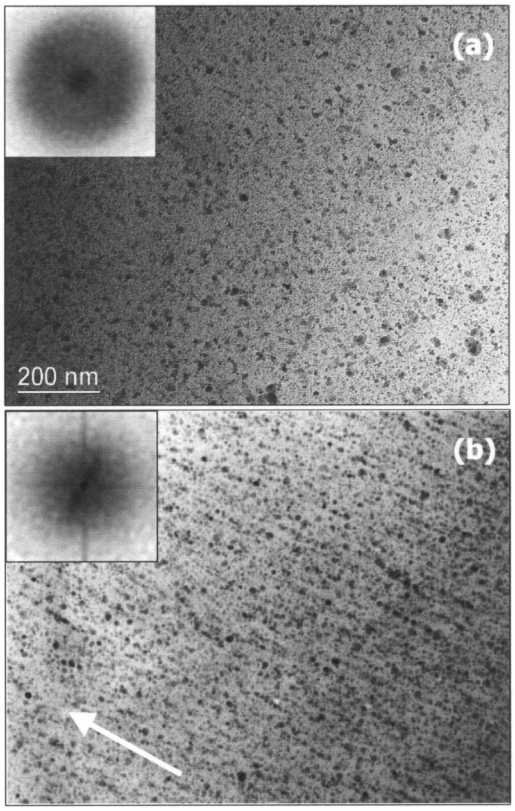

FIG. 2. Plan-view TEM images of Ag ion exchanged BK7 glass after 1 MeV Xe (a), and after subsequent 30 MeV Si irradiation (b). Scales of (a) and (b) are identical. The ion beam was under 60° off-normal and its projection onto the surface is indicated by an arrow. Clear alignment of Ag nanocrystals is observed along the ion beam direction. The insets show the spatial Fourier transform of the images (full scale $0.3\ \mathrm{nm}^{-1}$).

change. The Ag surface concentration is ~6 at. %, and the depth profile extends to 600 nm for a 7 min/310 °C ion exchange and to 1100 nm for a 10 min/350 °C condition. The projected range of 1 MeV Xe, i.e., the depth over which silver nanocrystals are formed, is 360 nm. Simulations[9] indicate that at an incoming angle of 60° the projected range of 30 MeV Si amounts to 4.8 μm, which is well beyond the depth of the ion exchanged region.

Optical transmission spectra were taken with a spectroscopic ellipsometer at normal incidence. Transmission electron microscopy (TEM) images were taken using a 400 keV electron beam. Preparation of plan-view TEM samples was done using a conventional backthinning method by polishing and ion milling using a 4 keV Ar ion beam under an angle of 6° with the surface.

Figure 1 shows the optical extinction versus energy of the samples made by the 7 min/310 °C ion exchange. After the initial Xe irradiation, the ion exchanged glass shows an extinction peak at 3.0 eV (410 nm), due to the surface plasmon absorption of Ag nanocrystals in a BK7 glass matrix (refractive index 1.61). This absorption band is polarization independent, as expected. From a fit of Mie theory to the spectrum,[7] it is estimated that approximately 11% of the Ag ions have agglomerated into nanocrystals. After Xe irradiation the glass shows a bright yellow color. After the subsequent irradiation with 30 MeV Si ions to a fluence of $2\times10^{14}/\mathrm{cm}^2$, the color of the glass changed to red and is now angle dependent. This is confirmed by the optical extinction measurements shown in Fig. 1, taken using normal-incident light polarized either parallel (open circles) or orthogonal (closed circles) to the direction of the Si beam projected onto the surface. Also shown in Fig. 1 is a reference measurement for a Ag ion exchanged sample that was irradiated with Si only; it does not show a plasmon absorption band and is colorless.

Plan-view TEM images are shown in Fig. 2, taken under normal incidence. Figure 2(a) shows the Ag nanocrystals formed after 1 MeV Xe irradiation, with typical diameters in the range 2–15 nm, randomly distributed in the glass. Figure 2(b) shows data taken after Xe and Si irradiations: randomly oriented Ag nanocrystals are observed, but in addition, arrays of aligned nanoparticles are found. These arrays are along the direction of the ion tracks (arrow). The redistribution of Ag is ascribed to the effect of the thermal spike of the 30 MeV ions, possibly in combination with anisotropic strain generated along the track.[10] The anisotropy is also observed in the spatial Fourier transform (inset) of Fig. 2(b), in contrast to that of Fig. 2(a). Note that no clear shape change is observed, as was seen for Au cores in silica colloids.[5]

The splitting of the plasmon bands observed in Fig. 1 can be explained by electromagnetic coupling among the aligned nanocrystals.[3] For polarizations parallel to the particle array, such coupling is known to result in a redshift. Conversely, transverse polarization will result in a blueshift. Finite difference time domain (FDTD) simulations of arrays similar to those observed in Fig. 2(b) show that the splitting due to the coupling can be well over 1 eV. As an example, a representative time snapshot of the electric field amplitude distribution obtained from FDTD simulation of a four Ag nanoparticle array is shown as an inset in Fig. 1. The strongly enhanced field between adjacent particles is indica-

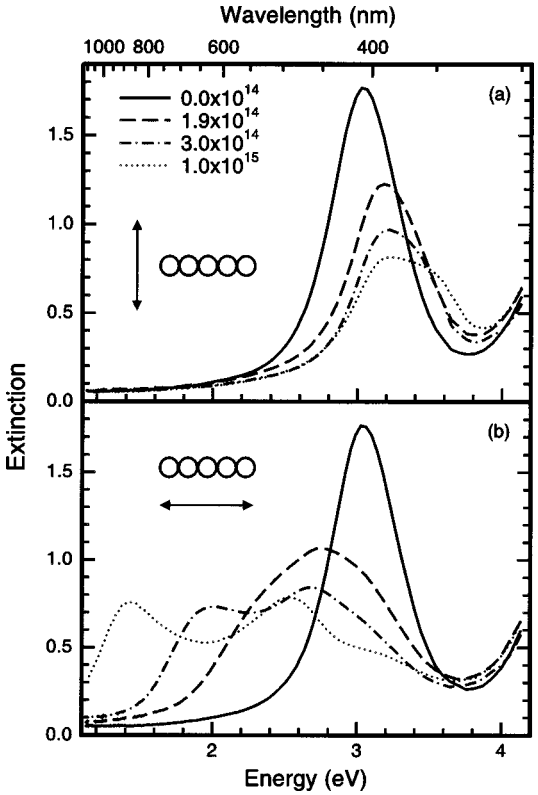

FIG. 3. Optical extinction spectra for Ag ion exchanged and Xe irradiated BK7 glass irradiated with 30 MeV Si at different ion fluences up to $1\times10^{15}/\mathrm{cm}^2$ (indicated in the figure). The polarization of the incoming light is transverse (a) or longitudinal (b) to the irradiation direction projected onto the surface. The splitting of the plasmon band can be tuned by changing the ion fluence and a shift well into the near-infrared is observed.

tive of strong interparticle coupling. Details of the simulation with quantitative results will be reported elsewhere.[11]

The plasmon band shift can be tuned by varying the Si ion fluence, as is illustrated in Fig. 3. Here optical extinction spectra are shown for Si fluences up to 1×10^{15} Si/cm^2 (10 min/350 °C). With increasing Si fluence, the plasmon absorption band for the transverse polarization is blueshifted [Fig. 3(a)], whereas the plasmon absorption band for the longitudinal polarization is redshifted [Fig. 3(b)]. At a fluence of 1×10^{15} Si/cm^2 a redshift by as much as 1.5 eV is observed, well into the near-infrared (870 nm). Another feature to notice in Fig. 3(b) is a second absorption band around 2.5 eV for high Si fluences. We attribute this to the formation and alignment of new Ag nanocrystals during the Si irradiation, and to the growth of existing nanocrystals. Note that after the original Xe irradiation, only 10% of the Ag ions are incorporated into nanocrystals, while 90% remain in solution. The slight difference in shape of the extinction spectra for Si fluences of $2\times10^{14}/\mathrm{cm}^2$ in Figs. 1 and 3 is attributed to different ion exchange conditions for the two cases, resulting in different Ag depth profiles. A next challenge is to further increase the Si ion fluence and investigate if the plasmon resonance can be shifted further, into the important telecommunication bands around 1.3 and 1.5 μm.

In conclusion, we have shown that 30 MeV Si ion irradiation of BK7 glass containing Ag nanocrystals induces a partial redistribution of the nanocrystals into linear arrays along the ion tracks. The anisotropy causes a splitting in the optical extinction spectra, so that different surface plasmon resonance bands for longitudinal and transverse polarizations are observed. Resonance shifts as large as 1.5 eV are observed, well into the near-infrared and are in qualitative agreement with a model for near-field electromagnetic plasmon coupling.

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