

## Annealing Effects on the Surface Plasmon Of MgO Implanted with Gold

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### ABSTRACT

Gold ion implantation was carried out with the energy of 1.1 MeV into (100) oriented MgO single crystal. Implanted doses are 1, 3, 6, 10  $\times 10^{16}$  ions/cm<sup>2</sup>. The gold irradiation results in the formation of gold ion implanted layer with a thickness of 0.2  $\mu\text{m}$  and defect formation. In order to form gold colloids from the as-implanted samples, we annealed the gold implanted MgO samples in three kinds of atmospheres: (1) Ar only, (2) H<sub>2</sub> and Ar, and (3) O<sub>2</sub> and Ar. The annealing over 1200°C enhanced the gold colloid formation which shows surface plasmon resonance band of gold. The surface plasmon bands of samples annealed in three kinds of atmospheres were found to be at 535 nm (Ar only), 524 nm (H<sub>2</sub>+Ar), and 560 nm (O<sub>2</sub>+Ar). The band positions of surface plasmon can be reversibly changed by an additional annealing.

### INTRODUCTION

The reduction of matter to nanometer dimension often leads to significant changes in optical, structural, and thermodynamic properties. The appearance of the surface plasmon (SP) resonance for metal colloid reduced to the nanometer scale is one example of how the optical properties of metals change when they are reduced in size. To form nanometer sized metal particles, we used ion implantation methods [1]. Metal colloid doped glasses, for example, show high optical nonlinearity, and are attractive candidates for utilization in optical devices [2,3]. The enhancement of the third order optical nonlinearity depends on the intensity and frequency of the SP resonance of the metal colloid. According to Mie's scattering theory and effective medium theory [4], we can predict the SP resonance frequency  $\omega_{\text{SP}}$  if we know the dielectric functions of the metal colloid  $\epsilon(\omega)$  and the host material  $\epsilon_m$ . As a first-order approximation, the following equation gives us the SP resonance frequency  $\omega_{\text{SP}}$ :

$$\epsilon(\omega_{\text{SP}}) + 2\epsilon_m = 0. \quad (1)$$

We have previously reported on the SP resonance of gold nanoparticles in the several substrates: sapphire, CaF<sub>2</sub>, and Muscovite mica [5]. MgO is also a material widely used in optics, such as windows and coatings. Although many of the alkaline earth oxides are hygroscopic and thus not widely used in optical systems, MgO is relatively insoluble, hard, and durable. Moreover, MgO is a good transparent material in the range between 300 nm and 7000 nm, and the optical absorption

edge has been measured to be about 7.77 eV (160 rim), Transition metals, for example  $\text{Fe}^{3+}$ , are common multivalent impurities in MgO with the order of 50 ppm. Absorption bands due to  $\text{Fe}^{3+}$  are found at 210 and 285 nm in MgO [8]. The F and F' absorption bands overlap in MgO, with the F peak occurring at 248 nm and F' peak at 252 nm. In MgO heavily damaged by ion bombardment, a broad absorption feature appears between the F band (-248 nm) and the fundamental absorption edge (-160 rim). Chen et al. reported [7] that mobile oxygen interstitial created by electron and neutron irradiation can be annealed out at 400°C, where the interstitial recombine with oxygen vacancies. On the other hand, the oxygen vacancies do not become mobile until the temperature reaches 1000°C [7]. In this paper, we mainly report on how the annealing atmosphere affects to the SP resonance.

## EXPERIMENTAL

MgO single crystals ( $15 \times 15 \times 0.5 \text{ mm}^3$ ) oriented (100) were obtained from two vendors (Harrick Scientific and Commercial Crystal Laboratories). The major impurities are  $\text{Fe}^{2+}$  of ~100 ppm and  $\text{Al}^{3+}$  of -40 ppm. The samples are implanted with 1.1 MeV gold  $^{197}\text{Au}^+$  with doses of 1, 3, 6,  $10 \times 10^{16}$  Au ions/cm<sup>2</sup>. The depth profile of gold concentration was measured by Rutherford Backscattering Spectrometry (RBS), using 2.4 MeV  $\alpha$  particles. Thermal annealing was carried out at temperatures between RT and 1200°C in a reducing (10% $\text{H}_2$ +90%Ar), an oxidizing (10% $\text{O}_2$ +90%Ar), and an inert atmosphere (100%Ar) flow.

The electronic spectra were measured between 185-3200 nm with a UV-Vis-NIR spectrophotometer (Hitachi, U-3 501). In order to study the annealing effects on Au implanted MgO, each transmission spectrum was taken every 15 min annealing, unless otherwise indicated. Indices of refraction of the samples were measured with an ellipsometer (Dudolph Research, 43603 -200E).

## RESULTS AND DISCUSSION

The RBS spectra show that the depth profile is, similar to the Gaussian distribution, whose peak of the Au concentration is located about 0.2  $\mu\text{m}$  from the surface (The spectra are not shown here).

The transmission spectra of as-implanted Au/MgO samples and an unimplanted MgO sample (called "virgin") are shown in Fig.1. The virgin sample (a) has a high transmission region (85% transmittance) down to 350 nm, and below 320 nm the transmittance suddenly drops due to  $\text{Fe}^{3+}$  ion impurities whose absorption bands are located at 285 nm and 210 nm. The spectra (b), (c), (d), and (e) are the transmission spectra for the gold implanted samples with dosages of 1, 3, 6, and  $10 \times 10^{16}$

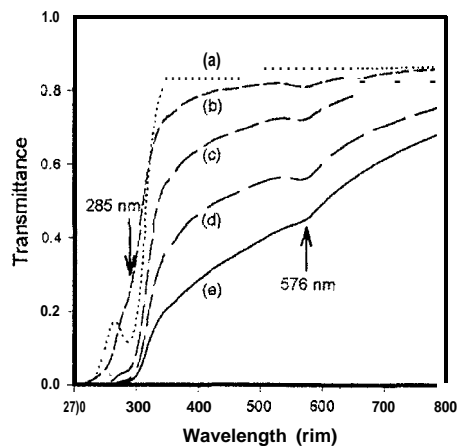


Figure 1 Transmission Spectra of (a) virgin MgO and as-implanted MgO with Au ions of (b)  $1 \times 10^{16}$ , (c)  $3 \times 10^{16}$ , (d)  $6 \times 10^{16}$ , and (e)  $10 \times 10^{16}$  ions/cm<sup>2</sup>.

ions/cm<sup>2</sup>, respectively. Every spectrum from (b) to (e) has a broad absorption band at 576 nm, which can be attributed to F-center (aggregates of F-centers) due to the irradiation damage by ion implantation [6]. As the gold dosage increases, the transmission decreases in the range between 300 nm and 1000 nm, mainly due to defects and scattering from small gold particles. The color of the as-implanted samples is dark brownish.

It has been reported that the bands around 250 nm and 355 nm are related to F-centers and F<sup>+</sup>-centers caused by neutron-irradiation, electron-irradiation and Mg-vapor-deposition [7]. The bands caused by neutron- and electron-irradiation can be annealed out at 600°C, while these bands generated by Mg-vapor-deposition could not be annealed out until the annealing temperature reaches 1200°C. The reason for this is as follows: in the sample, excessive Mg<sup>2+</sup> ions are introduced from Mg vapor and then the Mg ions migrate into the MgO bulk to cause oxygen ion vacancies. In this case there exist no interstitial oxygen ions in the system, while neutron- or electron- irradiated samples have interstitial oxygen ions to recombine to oxygen vacancies. The oxygen interstitial are mobile, while oxygen ion vacancies are immobile [7]. Below 300 nm, the Fe<sup>3+</sup> band is overlapped with the F- and F<sup>+</sup>-band, thus it is difficult to distinguish those bands in the as-implanted samples before annealing.

In Fig.2, two sets of spectra for sequentially annealed Au/MgO sample in both reducing and oxidizing atmospheres are shown, for the sample with the dosage of 6x10<sup>16</sup> ions/cm<sup>2</sup>. The annealing temperature and time for each spectrum are shown in Fig.2. The band at 576 nm disappeared after annealing at 400°C, as reported by Chen *et al.* [7]. Between 200°C and 1000°C, weak broad bands appeared around 340 and 365 nm. We will discuss these bands elsewhere. When the annealing temperature reached 1200°C, a strong broad band appeared at 524 nm for the samples annealed in the reducing atmosphere and at 560 nm for the oxidizing atmosphere, which are attributed to the SP resonance of gold colloids. As the annealing time increased at 1100- 1200°C, the SP bands became stronger, which indicates that at this temperature (1 100- 1200°C) the implanted gold ions begin to diffuse and aggregate to form metallic colloids. At the same time of colloid formation, the Fe<sup>3+</sup> band at 285 nm became weaker in the case of reducing atmosphere. It is also coincident that the temperature at which oxygen vacancies become mobile, as mentioned before.

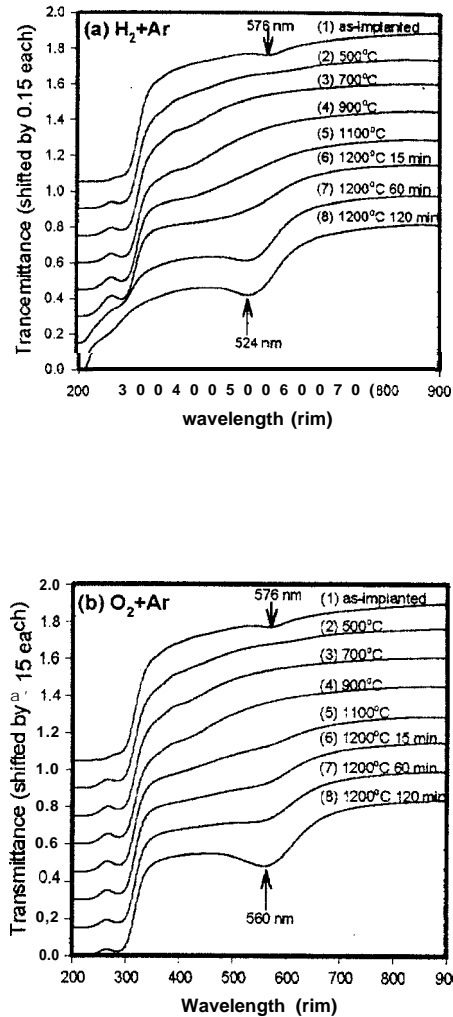
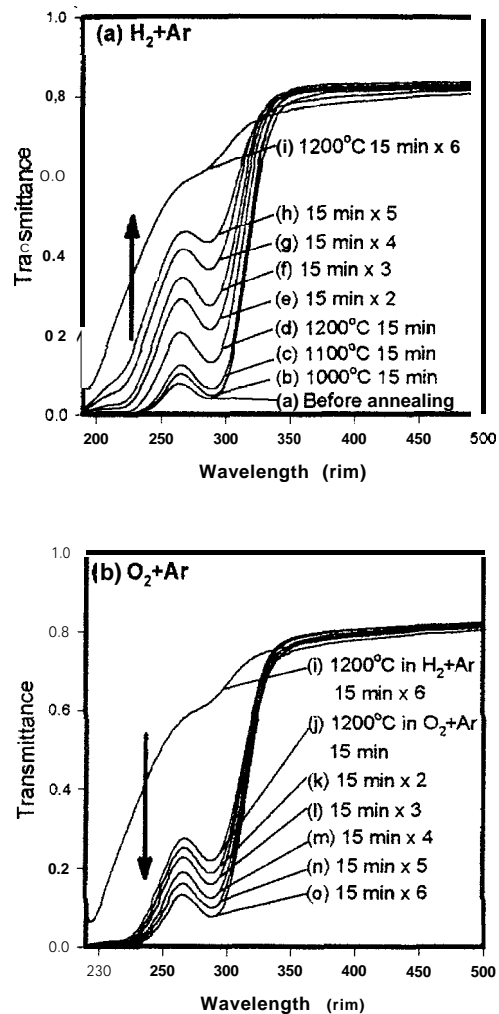


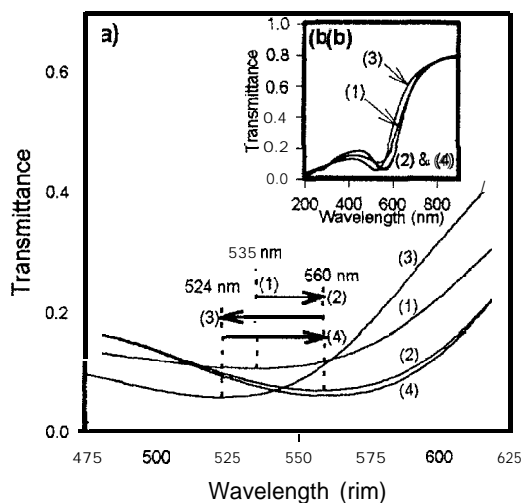
Figure 2 Transmission spectra of the sequentially annealed Au/MgO in (a)H<sub>2</sub>+Ar and (b)O<sub>2</sub>+Ar.

In order to investigate the correlation between the SP resonance and the reduction of  $\text{Fe}^{3+}$  band at 285 nm, we measured the transmission spectra of virgin MgO that was sequentially annealed in the similar way to the previously gold implanted samples. In Fig.3, (a) spectrum for virgin MgO is shown before annealing. Spectra (b), (c), and (d) are of the same sample after sequential annealing at 1000°C, 1100°C, and 1200°C, respectively, for 15 min. Spectra (e) to (i) are of the same sample additionally annealed at 1200°C for 15 min for each step. During annealing between 200°C and 900°C with a step of 100°C for 15 minutes each, the spectra did not exhibit any significant changes. After annealing at 1200°C for 90 minutes in total, (i) in Fig.3, the surface of the sample became slightly cloudy. However, before it became cloudy, the  $\text{Fe}^{3+}$  band at 285 nm became weak. Apparently, the  $\text{Fe}^{3+}$  ions were reduced to  $\text{Fe}^{2+}$  ions in the reducing atmosphere at high temperature, which resulted in an increased transmittance of 75% at 285 nm [8]. After annealing in a reducing atmosphere, we switched the atmosphere to  $\text{O}_2+\text{Ar}$ . The transmittance suddenly dropped just after annealing at 1200°C in oxidizing atmosphere for 15 minutes, as shown in Fig.3(b). Since we can assume that  $\text{Fe}^{3+}$  ions uniformly distributed in the entire sample, the reducing reaction occurs from surface to inside the sample until  $\text{Fe}^{3+}$  ions are almost completely converted to  $\text{Fe}^{2+}$  ions in reducing atmosphere. When annealing the samples in oxidizing atmosphere, the conversion from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  has taken place, as shown in Fig.3(b). However, this does not mean that both hydrogen and oxygen atoms diffuse into the sample. In the reducing atmosphere at high temperature, a hydrogen molecule takes an oxygen atom at the surface, leaving an oxygen vacancy with two electrons behind and giving one electron to an  $\text{Fe}^{3+}$  ion to form an  $\text{Fe}^{2+}$  ion. This reaction occurs only at the surface and will not continue inside the sample at lower temperature because oxygen vacancies are not mobile at low temperature ( $<1000^\circ\text{C}$ ). This is consistent with our observation that the spectra  $\text{Fe}^{3+}$  absorption decreases only at high temperature ( $\geq 1200^\circ\text{C}$ ). In the oxidizing atmosphere, oxygen vacancies are filled with oxygen and take electrons from  $\text{Fe}^{2+}$  to make them  $\text{Fe}^{3+}$  thereby allowing oxygen to diffuse into the sample when the temperature is high enough.



**Figure 3** Transmission spectra of virgin MgO annealed in (a)  $\text{H}_2+\text{Ar}$  and (b)  $\text{O}_2+\text{Ar}$  in the range for  $\text{Fe}^{3+}$  absorption band.

To confirm the annealing atmosphere dependence of the SF band position, we sequentially annealed an implanted sample (Au/MgO with dose of  $10 \times 10^{16}$  ions/cm<sup>2</sup>) at 1200°C in (1) Ar only, (2) O<sub>2</sub>+Ar, (3) H<sub>2</sub>+Ar, and (4) O<sub>2</sub>+Ar again for 2 hours each. Fig. 4 shows the vicinity (a) of the SP band and wider range of spectra in the inset (b). (1) After annealing in Ar only, SP appeared at 535 nm. (2) After annealing in O<sub>2</sub>+Ar, SP shifted to 560 nm. (3) Annealing in H<sub>2</sub>+Ar made SF shift to 524 nm. (4) Again, after annealing in O<sub>2</sub>+Ar, SP moved back to 560 nm. From these results, the SP position is reversibly depending on the annealing atmosphere. This reversibility suggests that the SP band position is influenced by the local dielectric constant of host near gold colloids. Once colloids with a certain size were formed, it is difficult to change their size or shape. Using these values of  $\omega_{SP}$  from experimental data, Eq. (1), and the optical constants of gold from literature [9], we calculated the local  $\epsilon_m$  to be 3.01 (Ar only), 2.45 (H<sub>2</sub>+Ar), and 3.90 (O<sub>2</sub>+Ar), while the standard value of  $\epsilon_m$  for MgO is 3.02.



**Figure 4** Shifts of surface plasmon bands due to different annealing atmospheres: (1) Ar only, (2) O<sub>2</sub>+Ar, (3) H<sub>2</sub>+Ar, and (4) O<sub>2</sub>+Ar at 1200°C for 2h each.

Inset (b) shows wide range of spectra.

## CONCLUSIONS

We have found that the annealing atmosphere affects the position of SF band of Au implanted in MgO. According to the temperature dependence of SF resonance development, oxygen vacancy mobility and reduction of Fe<sup>3+</sup> ions, the gold colloid formation must be well related to oxygen vacancy movement at high temperature. The shift and the reversibility may be useful for application to the development of nonlinear optical devices. Further study is needed to understand the mechanism of the annealing effects on surface plasmon bands.

## ACKNOWLEDGEMENTS

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