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Study of the Effects of MeV Ag and Au Implantation on the Optical Properties of $LiNbO_3$.

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Abstract.

We present the results of characterization of linear absorption and nonlinear refractive index of Au and Ag nanoclusters made by MeV ion implantation into $LiNbO_3$. Ag was implanted at 1.5 MeV to fluences of 2 to 17 x $10^{16}/cm^2$ at room temperature. Au was implanted to fluences of 5 to 20 x $10^{16}/cm^2$ at an energy of 2.0 MeV. Optical absorption spectrometry indicated an absorption peak at 560 nm for the Au implanted samples after a 30 minute heat treatment at 500°C in air. The peak shifted to ~620 nm after heat treatment at 1000°C. The Ag implanted samples had absorption peaks at 445 to 485 nm before heat treatment. After 500°C heat treatment for 1 h the peaks decreased in height and shifted to 545 to 560 nm. Heat treatment at 800°C was sufficient to return the Ag implanted crystals to a clear state. The size of the clusters was determined from the absorption peaks. The Ag clusters did not change appreciably in size with heat treatment. The Au clusters increased from 1 to 3 nm upon heat treatment at 1000°C. Measurements of the nonlinear refractive indices were carried out using the Z-scan method with a tunable dye laser pumped by a frequency doubled mode-locked Nd:YAG laser. The dye laser had a 4.5 ps pulse duration time and 76 MHz pulse repetition rate (575 nm).

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constant of the bulk metal. Equation 1 has a maximum value at the surface plasmon resonance frequency (ω_p), where

$$\varepsilon_1(\omega_p) + 2n_o^2 = 0\ . \tag{2}$$

If the volume fraction Q of the colloids is large Eq. 2 becomes [1]

$$\varepsilon_1(\omega_p) + \tfrac{2+Q}{1-Q} n_0^2 = 0 \tag{3}$$

Using the tabulated values [14,15] of ε_1 for Ag and Au as a function of the photon wavelength, and using $n_0 = 2.2$, Equation 2 predicts that the wavelengths for the surface plasmon resonance frequencies should appear at 520 nm for Ag and 620 nm for Au. Equation 3 predicts that increasing volume fraction results in a red shift of the absorption peak.

If the metal spheres are small compared with the wavelength of the incident light, their radius estimated from the optical absorption spectrum is $r = v_f/\Delta\omega_{1/2}$ [1], where v_f is the Fermi velocity of the metal and $\Delta\omega_{1/2}$ is the full width at half maximum of the absorption band.

Experimental Procedures.

Single crystal, 1mm thick $LiNbO_3$ wafers were obtained from Crystal Technology Inc., (Palo Alto, CA). We used 1.5 MeV Ag and 2.0 MeV Au with beam currents of 2 to 3 $\mu A/cm^2$ and the samples were maintained at room temperature. Ag was implanted to fluences ranging from $2 \times 10^{16}/cm^2$ to $1.7 \times 10^{17}/cm^2$ while Au was implanted from $5 \times 10^{16}/cm^2$ to $2.0 \times 10^{17}/cm^2$.

Optical absorption photospectrometry was done soon after implantation and immediately after heat treatment using a Cary model 3e spectrophotometer. Heat treatments were done in air at temperatures of 500°C to 1000°C for times from 0.5 to 14 hours. Average radii were measured from these spectra.

To measure the third order nonlinear optical coefficient, n_2, we used the z-scan technique [17, 18] employing a tunable pulsed dye laser pumped by a frequency doubled mode locked Nd:YAG laser run to give a wavelength of 575 nm and a pulse width of 4.5 ps at a repetition rate of 76 MHz. The average power was 70 to 350 mW, giving a power density applied to the sample in the range of 0.02 to 0.1 GW/cm^2.

RESULTS and DISCUSSION.

The damage and modification of the optical properties are directly proportional to the atomic number and fluence of the bombarding ion [19, 20]. The $LiNbO_3$ samples implanted with Ag at fluences of less than 8 x 10^{16}/cm^2 were brownish immediately after implantation but turned blue after 1 hr heat treatment at 500°C, whereas a sample implanted at 1.7 x 10^{17}/cm^2 remained almost black. The gold samples were much darker and changed to a dark purple after heat treatment at temperatures above 700°C. Within a week of implantation, and prior to heat treatment, precipitates appeared on the surfaces of both the Ag and Au implanted samples, as was expected [21,22]. EDX analysis of the precipitates gathered on a strip of carbon tape from the surface confirmed that both Au and Ag were being expelled to the surface. The surface coverage of the Ag precipitates was proportional to the fluence. For the highest fluence Ag implanted sample most of the surface was covered by Ag. At 5 x 10^{16}/cm^2 droplets of Ag of various sizes appeared. At the lowest fluence, 2 x 10^{16}/cm^2, the crystal surface was covered with Ag in a dendritic growth pattern. The precipitates were removed prior to heat treatment with a methanol soaked wiper and did not reappear. The surfaces of all of the Ag implanted samples were also noticeably textured by the implantation; the higher fluence samples even functioned as poor quality diffraction gratings. The Au implanted $LiNbO_3$ also showed some surface texturing but not to the same extent as the Ag samples. The texturing remained in the 2 x 10^{17} Au/cm^2 sample after 10 hours at 1000°C.

The absorption spectra from a Ag implanted sample at a fluence of 5 x 10^{16}/cm^2 is shown in Figure 1. The absorption peaks decreased in height and shifted to longer wavelengths, with the greatest shift occuring during the initial 500°C heat treatment. After 800°C heat treatment the 2 x 10^{16} Ag/cm^2 implanted sample's absorption spectrum was indistinguishable from that of a virgin crystal. The change in height of the spectra may be due to a reduction in the number of Ag clusters as Ag diffuses atomistically into the substrate. The wavelengths of the Ag absorption peaks and the radii of the clusters are shown in Table 1 for each fluence and heat treatment. The radii are initially the same for all three fluences, then increase from 30 to 60 percent after heat treatment. Another increase in radius is seen just before the aborption spectra disappear.

In the as-implanted state the absorption peaks were at a wavelength shorter than that expected from theory (~520 nm). The shift toward longer wavelength could be due to changes in the volume fraction as indicated by Equations 2 and 3 if clusters in less densely Ag populated regions dissolve more quickly than those in regions with higher Ag concentration. Another likely contributing factor to the red shift is that the heat treatment is removing implantation damage[23]. $LiNbO_3$ implanted with Ag 1 x 10^{17}/cm^2 at 190 keV has been shown to undergo full epitaxial regrowth after heat treatment at 400°C [24] but an anneal of 800°C for 1 h is necessary for full removal of the implantation damage. At the end of range ions implanted into $LiNbO_3$ have been shown [23, 25] to decrease the index of refraction by over 5 percent. From Equation 3, changing the host index by 5 to 10 percent would result in a shift of the expected absorption peak of 20 to 40 nm.

The absorption spectra for a 9 x 10^{16} Au/cm^2 implanted sample is shown in Figure 2. No absorption peak is visible prior to heat treatment. There was little change in the spectrum from the 5 x 10^{16} Au/cm^2 sample after 0.5 and 14 h at 500°C but for higher fluence samples (9 x 10^{16}/cm^2 and 2.0 x 10^{17}/cm^2) the 500°C for 0.5 h heat treatment resulted in an absorption spectrum typical of Au. At 600°C the absorption peak shifts to longer wavelengths and decreases in height. At 700°C and above the peak positions continue to shift to longer wavelengths but increase dramatically in height. A similar, but larger, peak growth and decay with a red shift was noted at 500°C by Shang, et. al. [21] for Au implanted into $LiNbO_3$ at 23 keV. In their case heat treatment at 600°C for up to 8 hr resulted in a blue shift and a large decrease in the peak height with the expectation that the absorption spectrum would disappear with further heat treatment, as is the case for Ag in $LiNbO_3$. Shang, et. al. concluded that there may be a certain temperature (about 500°C) below which the colloids attract gold atoms that have not become part of a cluster and above which the gold escapes from the clusters and diffuses into the host. Our spectra show that this is not the case for MeV Au implanted into $LiNbO_3$. The absorption peaks and radii for 2.0 MeV Au implanted $LiNbO_3$ are shown in Table 2 for heat treatment temperatures up to 1000°C. The clusters begin to grow significantly larger at 800 to 900°C and appear to reach a maximum size at 1000°C. The peak height slowly decreases at 1000°C and the red shift continues for the lower fluence implantations.

The results of the z-scan are shown in Table 3. The thickness of the colloidal layer used in the calculation of n_2 (240 nm for 1.5 Mev Ag and 180 nm for 2.0 MeV Au) was estimated using

SRIM96 [16]. The nonlinear index is the average of five scans at different laser powers, except for the two samples heat treated to 800°C, which are single runs. The magnitude of the nonlinear index increases with increasing fluence and optical density. For the Ag implanted samples heat treated to 800°C the absorption spectrum is equivalent to or very close to that of the virgin substrate yet a significant nonlinear index is seen. This is not the intrinsic nonlinear index of $LiNbO_3$, which is negative, as was confirmed by a z-scan of an unimplanted area. The nonlinear indices reported here are at least one order of magnitude greater than those reported for other silver clusters in the literature [26]. This indicates the presence of the cumulative thermal self-focussing effect which can still occur for the short pulses used in this work due to the relatively high pulse repetition rate (76 MHz versus 3.8 MHz in Ref. [26]).

CONCLUSIONS

Some fraction of the Ag and Au implanted at 1.5 and 2.0 MeV, respectively, into $LiNbO_3$ was expelled from the crystal at room temperature within a week of implantation. The Ag and Au implanted $LiNbO_3$ reacted differently to heat treatment as observed in the optical absorption spectra. Silver clusters disappeared quickly at a heat treatment temperature of 800°C. Au clusters from 2.0 MeV implantation grew at heat treatment temperatures up to 1000°C. Heat treatment of the Au implanted samples was necessary to see the expected absorption spectrum from Au clusters. The z-scan, however, indicated a substantial nonlinear index from a sample prior to the absorption spectrum becoming clearly defined. For Ag implanted $LiNbO_3$ the Ag absorption peak appears without heat treatment and disappears upon heat treatment at 800°C but enhancement of the nonlinear index remains after reduction of the absorption. The z-scan indicated that implantation of Ag and Au in $LiNbO_3$ creates a composite that exhibits a Kerr-type nonlinear susceptibilty.

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Figure Captions

Figure 1. Optical density vs. wavelength for $LiNbO_3$ implanted with 5×10^{16} Ag/cm^2 at 1.5 MeV for heat treatments of 500 to 800°C for times indicated.

Figure 2. Optical density vs. wavelength for $LiNbO_3$ implanted with 9×10^{16} Au/cm^2 at 2.0 MeV for heat treatments of 500 to 1000°C for times indicated.

Table 1. Wavelengths of absorption maxima and corresponding cluster radii for Ag implanted $LiNbO_3$ at 1.5 MeV at indicated fluences and heat treatments.

Ag	Fluence, ion/cm^2	2×10^{16}		5×10^{16}		1.7×10^{17}	
Temp., °C	Time, hr.	λ_{max}, nm	r, nm	λ_{max}, nm	r, nm	λ_{max}, nm	r, nm
RT		443	1.1	446	1.1	485	1.0
500	1	542	1.3	532	1.6	520	1.25
600	0.5	542	1.25	543	1.5	556	1.25
700	0.5	546	1.3	548	1.6	564	1.2
700	1	544	1.5	549	1.6	559	1.2
800	1	none	none	540	1.9	544	1.5

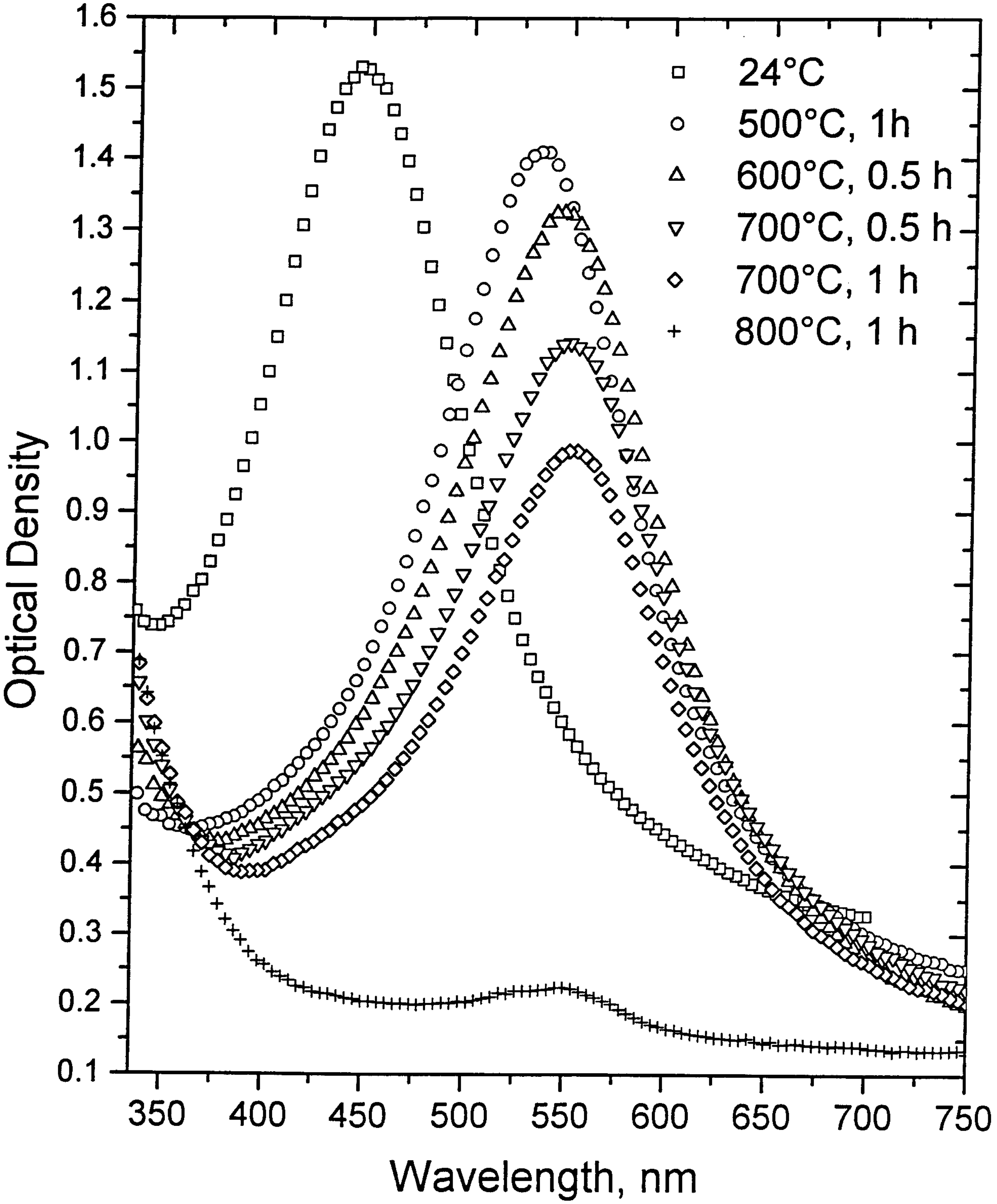
Table 2. Wavelengths of absorption maxima and corresponding cluster radii for Au implanted $LiNbO_3$ at 2.0 MeV at indicated fluences and heat treatments.

Au	Fluence, ion/cm^2	5×10^{16}		9×10^{16}		2×10^{17}	
Temp., °C	Time, hr.	λ_{max}, nm	r, nm	λ_{max}, nm	r, nm	λ_{max}, nm	r, nm
500	0.5	none	none	554	0.9	560	1.0
500	14	none	none	570	0.8	583	0.9
600	1	553	0.6	585	0.8	592	1.0
700	1	595	1.2	603	1.2	605	1.1
800	1	603	1.4	608	1.3	612	1.5
900	1	605	2.0	612	1.8	617	1.8
1,000	1	608	3.0	612	2.6	630	2.5
1,000	4	612	3.0	615	2.6	629	2.5
1,000	10	617	3.0	619	2.9	630	2.6

Table 3. Nonlinear refractive index at 575 nm for 1.5 MeV Ag and 2.0 MeV Au implanted $LiNbO_3$ heat treated at 500°C and 800°C.

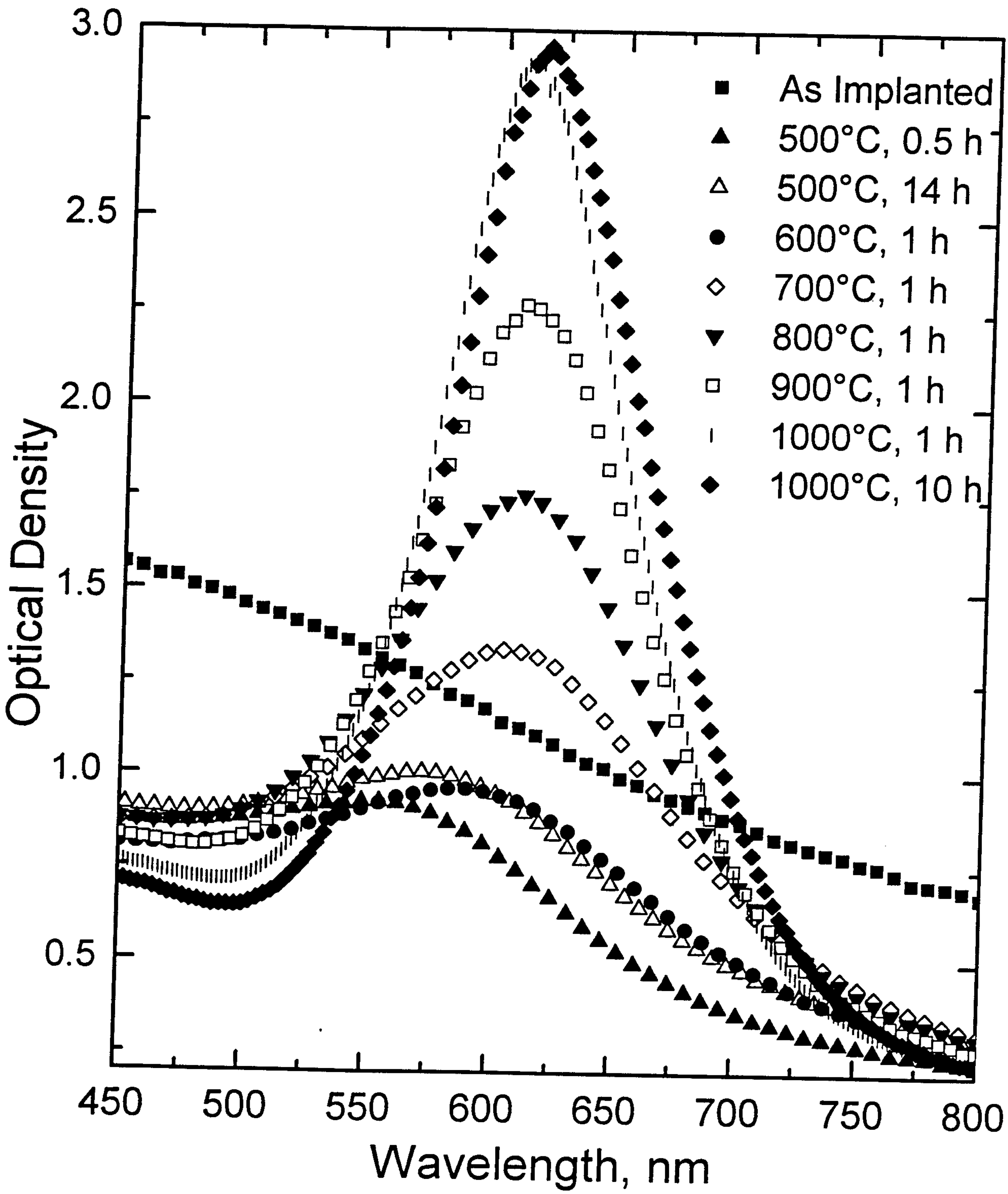
Ion	Fluence, ions/cm^2	Time	Temp °C	Optical Density at 575 nm	Nonlinear index, n_2, 10^{-8} cm^2/W
Ag	2×10^{16}	1 hr	500	0.39	0.96
		1 hr	800	0.15	0.35
Ag	5×10^{16}	1 hr	500	1.0	2.90
		1 hr	800	0.2	0.38
Ag	17×10^{16}	1 hr	500	1.87	6.81
Au	5×10^{16}	14 hr	500	0.46	2.18
Au	9×10^{16}	14 hr	500	1.01	5.97
Au	9×10^{16}	0.5 hr	500	0.9	4.37
Au	20×10^{16}	14 hr	500	1.96	16.5

Figure 1.



□ 24°C
○ 500°C, 1h
△ 600°C, 0.5 h
▽ 700°C, 0.5 h
◇ 700°C, 1 h
+ 800°C, 1 h
Optical Density
Wavelength, nm
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
350
400
450
500
550
600
650
700
750

Figure 2



Optical Density
Wavelength, nm
3.0
2.5
2.0
1.5
1.0
0.5
450
500
550
600
650
700
750
800
■ As Implanted
▲ 500°C, 0.5 h
△ 500°C, 14 h
● 600°C, 1 h
◇ 700°C, 1 h
▼ 800°C, 1 h
□ 900°C, 1 h
ı 1000°C, 1 h
◆ 1000°C, 10 h

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