Cu Nanoparticle Grating Fabricated by Negative Heavy-ion Implantation

Haisong Wang, Oleg A. Plaksin*, Jing Lu and Naoki Kishimoto

Nanomaterials Laboratory, National Institute for Material Science, 3-13 Sakura, Ibaraki, 305-0003, Japan

Fax: 81-29-863-5571, e-mail: WANG.Haisong@nims.go.jp

*SSC RF-IPPE, Obninsk, 249033, Russia

Fax: 81-29-863-5571, e-mail: Oleg.PLAXINE@nims.go.jp

Grating with the smallest periodic constant of 2 μ m and line width of less than 1 μ m inside the SiO₂ was obtained by heavy ion implantation method using photo resist film as the mask. Results of absorbance measurement showed the surface plasmon peak around 2.0 eV, which proved that the Cu nanoparticles formed in the implanted area during ion implantation. The absorption character of gratings with different periodic constant and implantation parameter described the precipitation process for nanoparticles. Further optimization of technology is possible to develop the grating structure, whose period constant is at the level of nanometer. The variation in transmitted diffraction pattern was expected theoretically when the nonlinear effect induced by nanoparticles was excited, which could be applied to switching in optical communication. Key Words: Ion implantation, Cu nanoparticle, Grating

1. INTRODUCTION

In recent years, metal nanoparticles composites and the structures based on them have attracted much attention in the world [1-3]. The metal nanoparticle in insulator, for example, SiO₂, induces the surface plasmon resonance (SPR) peak in the absorbance spectrum. Furthermore, the nonlinear effect will be excited when the composites are irradiated by strong incident light, with the response time of several pico-seconds. This property could be applied to the optical switching system. Currently, ion implantation is one of the most favorable techniques to fabricate the metal nanoparticles in the insulator substrate, owing to its controllability and flexibility. Using this technique, we carried out the research focused on all kinds of nanoparticles in insulators and their properties, which were shown in the references [4-6].

In this paper, the grating inside the SiO₂ (KU-1TM) substrate, consisting of nanoparticles, was developed by the Cu ion implantation method using a photoresist film as the mask. The grating has a periodic constant of 2 μ m at minimum and line width of less than 1 μ m. The formation of nanoparticles inside the substrate depended on the parameters of ion irradiation and grating line width. The variation in transmitted diffraction pattern was expected theoretically when the nonlinear effect induced by nanoparticles was excited, which could be applied to optical switching in communication.

2. EXPERIMENTAL

The grating pattern, made by photoresist film was deposited on the SiO₂ (KU-1TM) substrate by lithography technique before the subsequent Cu heavy-ion irradiation. The grating periodic constants used were 2 μ m, 3 μ m

and 12 μ m. The corresponding line widths of those gratings were 1 μ m, 1.5 μ m and 6 μ m, respectively. The common photoresist was applicable in the case of low energy ion irradiation.

The ion irradiation was carried out with the energy of 60 keV. The total fluence changed from 3×10^{16} ions/cm² to 2×10^{17} ions/cm², as well as the flux from $3 \,\mu$ A/cm² to $10 \,\mu$ A/cm² in order to obtain the nanoparticles with different morphology. Annealing was a selective step to collect the Cu ion and form nanoparticles. After removing the photoresist mask, the sample with grating was ready for characterization.

Steady-state absorption properties of those gratings were measured using a dual beam spectrometer. The surface plasmon resonance (SPR) peak around 2.0 eV should be found if Cu nanoparticles appeared in the substrate, corresponding to the formation of nanoparticle. The grating characteristics of transmitted diffraction pattern were examined by using a He-Ne laser system (wavelength: 632.8 nm).

3. RESULTS AND DISCUSSION

The surface morphology of the substrate was measured by using a profile meter, after removing the mask. As far as the sample with the implanted fluence of 2×10^{17} ions/cm² was concerned, the relative height between the implanted area and un-implanted area was about 1 nm, which resulted from the etching effect (sputtering) during the ion implantation would not affect the grating effect. The ion implanted area located at several ten nanometers depth below the substrate surface, but we still can observe it by optical microscope because the SiO₂ layer is transparent.

The top view pictures of several samples with

different periodic constant, taken by CCD, were shown in Fig. 1. In these pictures, the gray area represents the ion-implanted region, while the dark green area corresponds to the region protected by mask. The border of the two regions was fairly distinct. Figure 1 (a) showed the grating with periodic constant of 2 μ m. The line width of implanted area was around 1 μ m. Figure 1(b) showed the case that the period constant was 3 μ m, whose line width of implanted area was more than 1 μ m.







Fig. 1. Grating picture with different periodic parameter. (a) Periodic constant of $2 \mu m$ (b) Periodic constant of $3 \mu m$.

It was difficult to directly obtain the absorbance of implanted area, making use of the dual beam method. But we could estimate it approximately. In the case of measuring a grating, the average intensity we measured was contributed by both of the implanted area and the area without being implanted. As a solution, the reflected intensity and transmitted intensity could be calculated by using the average intensity we measured on this grating sample and the results on SiO₂ substrate. Finally, the absorbance of the implanted area was obtained by calculation. This approximation method is valid for the grating with a small periodic constant, which would not affect displaying the SPR peak in the absorbance spectrum. The measured absorbance of grating with 3 μ m periodic constant was shown in Fig. 2.

The SPR peak around 2.2 eV indicates the Cu nanoparticles in the grating, fabricated by the condition of 10 μ A flux and 2×10¹⁷ ions/cm² fluence. The jitter peak at 1.4 eV is resulted from system error of our facility. The SPR peak in the absorbance spectrum is weak, compared with the sample without grating fabricated at



Fig. 3. Absorption spectrum at $1\mu A 6 \times 10^{16} \text{ions/cm}^2$.

the same implantation condition. The ion distribution lack in longitudinal direction (in Fig. 1) weakens the formation of nanoparticles. Figure 3 showed the absorbance spectrum of the sample with the same periodic constant but different implantation parameters, which were a flux of 1 μ A and a fluence of 6×10^{16} ions/cm². The SPR peak we obtained was slighter than that of the sample mentioned above, probably resulted from the smaller size of nanoparticle. In case that the ion irradiation is performed on the condition of weak flux, implanted ions diffuse more wide than that by strong flux irradiation. The density of ions would determine the



Fig. 4. Absorption spectrum before and after annealing.



Fig. 5. Top view of the grating after annealing.

morphology of nanoparticle.

Annealing was a selective and effective method to promote nanoparticles formation. However, it also may results in diffusion of nanoparticles because of the ion distribution difference in longitudinal and transverse direction. Figure 4 showed the absorption spectrum results of the grating with $2 \mu m$ period on the implantation condition of $10 \mu A/cm^2$ flux and 1×10^{17} ions/cm² fluence, before and after the annealing by 600°C for 1 h. The strong SPR peak only appeared after the annealing, as shown in Fig. 4. Simultaneously, the diffusion effect of the nanoparticle made the border of the grating indistinct. The nanoparticles were found in the area without ion implantation, as shown in Fig. 5. The furthermore optimization on annealing is possible to improve the nanoparticle formation.

The transmission properties for these kinds of gratings without being annealed were measured by He-Ne laser, which was shown in Fig. 6.



Fig. 6. Transmission property of gratings with different period.

4. TRANSMITTED DIFFRACTION PAITERN

The grating structure, as shown in Fig. 7, was different from the conventional grating. The thickness t of the nanoparticle layer was about 50 nm, and the period d of the grating was 2 μ m. Furthermore, it should be noted that, within the sample, the total internal reflection would occur at a diffraction angle θ_{max} , which was

$$\sin \theta_{\max} = \frac{1}{n_{SiO_{+}}} \tag{1}$$

Using the grating equation and expression (1), we could easily calculate the order in the transmitted diffraction pattern. The results accorded well with the results measured, as shown in Fig.6 (b) and (c).



Fig. 7. Schematic of grating calculation.

As far as one point A in the interface of the sample is concerned, whose diffraction angle is θ , the total complex amplitude was contributed by both of the nanoparticles area and the SiO₂ area, written as

$$\widetilde{U}_{total}(\theta) = \widetilde{U}_{SiO_2}(\theta) \cdot \exp(i\Theta) + \widetilde{U}_{nano}(\theta)$$
(2)
in which,
$$\widetilde{U}_{SiO_2}(\theta) = A_0 e^{i\varphi_1(\theta)} \frac{\sin(N\beta_2)}{\sin(\beta_2)} \int_{-a/2}^{a/2} \widetilde{U}_2(x) \exp(-ik_2 x_j \sin\theta) dx_j$$

$$\widetilde{U}_{nano}(\theta) = A_0 e^{i\varphi_1(\theta)} \frac{\sin(N\beta_2)}{\sin(\beta_2)} \int_{-b/2}^{b/2} \widetilde{U}_1(x) \exp(-ik_2 x_j \sin\theta) dx_j$$
$$\Theta = \left[\frac{d}{2}\sin\theta + (n_{nano} - n_{sio_2})\frac{t}{\cos\theta}\right] \frac{2\pi}{\lambda_2}$$
$$\beta_2 = \frac{\pi}{\lambda} d\sin\theta$$

Here, λ_2 was the wavelength of the light source in SiO₂ region, and N was the quantity of the slots. Diffraction angle θ should be less than θ_{max} . $\varphi(\theta)$ indicates optical path from center of grating to the point A. Function $\tilde{U}(x)$ shows the profile of transparency in SiO₂ region or implanted region, respectively. Here, we consider it as 1 in the integral region (a, b means the width of un-implanted region and implanted region, respectively) to simplify calculation. Term $\exp(i\Theta)$ in eq. (2) is owing to the additional contribution of optical path difference between implanted layer aperture and SiO₂

aperture. It is easy to calculate the diffraction patterns of different gratings. For example, Fig. 8 shows the diffraction pattern in terms of grating with 2 μ m period constant. Logarithmic coordinate is adopted to decrease the contrast of intensity between different peaks. The relative location and quantity of peaks corresponds to Fig. 6 well. In our calculation, we neglect the absorption resulted from implanted layer. In case of considering absorption, the pattern would not change except the value of transmitted intensity.

As described in many reports, the nonlinear effect could be excited by strong light and the refractive index would vary. Calculated result indicates the intensity of transmitted pattern would change when the optical path difference was changed. Figure 9 shows this variation at the center of diffraction pattern in respect to nonlinear refractive index with different implanted layer thickness t (μ m). By optimizing the implantation parameters and the nanoparticles elements, it is possible to enhance this effect, which is useful in optical communication as a switching device.



1g. 9. Intensity at the center of transmitted pattern versus nonlinear refractive index.

5.CONCLUSION

The gratings formed by Cu nanoparticles were obtained by heavy ion implantation using a photoresist as the mask. The characteristics of gating with different implantation parameters were compared, which show different property from common transmitted grating and provide the reference data for optimization in the future. The variation of intensity on diffraction pattern excited by strong light was also predicted which may be applied to optical switching in communication.

ACKNOWLEDGEMENT

The author would like to express the appreciation to Dr. Amekura and Dr. Fudamoto for their kind assistance in the experiments. He also appreciates Dr. Junfeng Song, the associate professor in Jilin University, P.R.China for his useful discussion.

REFERENCE

[1] F. Hache, D. Ricard, C. Flyzanis, U. Kreibig, *Appl.Phys.Lett.*, A, **47**, 347-57 (1998)

[2] J. Stehr, J.Crewett, F. Schindler, R. Sperling, GV. Plessen, U. Lemmer, J. M. Lupton, T. A. Klar, J. Feldmann, A. W. Holleitner, M. Forster, U. Scherf, Adv. Mater., 15, 1726-1729 (2003)

[3] M. Salerno, N. Felidj, J. R. Krenn, A. Leitner, F. R. Ausssenegg, *Phys. Rev.*, B, **63**, 165422 (2001)

[4] Y. Takeda, C. G. Lee, V. V. Bandourko, N. Kishimoto, *Mater. Trans.*, **43**, 1057-60 (2002)

[5] N. Kishimoto, V. T. Gritsyna, Y. Takeda, C.G. Lee, J. Surf. Sci., 4, 220-25 (1998)

[6] H. Amekura, N. Umeda, Y. Takeda, J. Lu, N. Kishimoto, *Appl.Phys.Lett.*, **85**, 1015-17 (2004)

(Received December 24, 2004; Accepted March 25, 2005)