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Second-order nonlinearity of doped H:SiO$_2$ films prepared by Matrix Distributed Electron Cyclotron Resonance and irradiated by electron beam

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Amorphous N-doped H:SiO$_2$ films on silica prepared by Matrix Distributed Electron Cyclotron Resonance method were irradiated by electron-beam with different doses. With Maker fringe measurements, second-harmonic generation was observed in the irradiated regions and the films exhibited a maximum second-harmonic signal under the 5 μA/cm^2, 480s irradiation condition. The magnitude of the induced second order nonlinear coefficient d_{33} is of the order of 0.003 pm/V. The d_{33} is small but the striking feature is the observation of a surface level shift connected to electron-beam poling with topography measurements. The surface level shifts increased with the increasing of electron doses in both X and Y directions, which fact was related to the implanted electron, dose. With different temperature for an annealing time of 1/2h, the surface level shifts in both X and Y directions increases firstly and got the maximum change at 300 °C, and then decreases when the temperature was increased. In the same time, the second-harmonics (SH) signal decreased to zero. The surface was recovered at the temperature of 1250 °C, which means that there was no matter loss with electron-beam writing in the films. The second harmonic generation in the films is caused by the frozen-in electric field induced by the charge implantation from the electron-beam (second order non linear coefficient $\chi^{(2)}$ is proportional to this electric field). The strength of the electric field is determined by two conditions: the trapping centers (numbers, depth) and the remaining conductivity under large electric field.

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1. Introduction

Recent studies have shown that electron beam poling can induce second-harmonic generation (SHG) in amorphous materials, especially in glasses [1-3]. It is well known that second-order susceptibility should be zero and second-harmonic generation is consequently forbidden in the centrosymmetric materials or amorphous materials. However, Sasaki *et al.* [4] and Osterberg *et al.* [5] have observed SHG in glass fibers and bulk glasses, which means that the centrosymmetry has been broken by poling treatment and SHG was induced. And, then, more and more researchers try to find the second-order nonlinear optical materials by different poling techniques and attempts are in progress to achieve waveguides for second-harmonic waves using amorphous materials especially low-cost glasses. So it is urgent presently to search for some new SHG materials especially SHG film materials for waveguide applications in optical communications and integrated optics. The nonlinear silica and silicate glasses will be one promising nonlinear materials because of their easy fabrication processes, low optical loss and high transparency, especially low cost, which stimulate much interest for waveguide-type optical devices applications such as electro-optic modulators, routers, switches and nonlinear optical parametric converters. In this paper, with electron beam current of 50 nA, second-harmonic generation was observed in the N-doped H:SiO$_2$ films with the Maker fringe measurements [6] and the surface level shift was also observed with interferometer microscope measurements.

2. Experimental details

The amorphous N-doped H:SiO$_2$ films consisted in a 5 μm layer of N-doped silica, deposited on a 1 μm buffer layer of pure SiO_2, on a silica (Suprasil®) substrate elaborated by the MDECR-PECVD. The results of chemical analysis by EPMA gave a uniform composition of 52.6 wt% (64.8 at%) of O, 44.7 wt% (31.5 at%) of Si, 2.5 wt% (3.7 at%) of N and 0.2 wt% (5 at%) of H. The films were used further without thermal annealing.

The films were covered with an Ag conductive film because we have observed that mirror effect developed in the irradiation dose range for obtaining SHG. The irradiation was performed with a SEM (Scanning Electron Microscope). The irradiation conditions are shown in Table 1.

Table 1. Irradiation conditions used in our experiments. Accelerating voltage: 25 kV; Irradiated area: 1 mm^2; Incident current: 50 nA.

Experiment #	Time (s)	I (nA)	Dose (μC/cm^2)
1	30 (0.5')	50	150
2	60 (1')	50	300
3	120 (2')	50	600
4	240 (4')	50	1200
5	480 (8')	50	2400
6	960 (16')	50	4800

The irradiated film surface was observed by phase shift interferometer microscope (Texas USA) with the ×10 objective lens before and after cleaning the conductive Ag film. The Maker fringe method was used to measure SHG.

3. Results

3.1 Second-harmonic generation

From another study [7], an estimate of the dose necessary for saturating the electric field has been deduced. We have also performed a range of irradiation doses and Maker fringes were observed in the irradiated region excepted for #1 [6]. Fig. 1 shows the Maker fringe of #5 irradiated position. It is seen from Fig. 2 that the largest SHG is obtained in the #5 irradiated position.

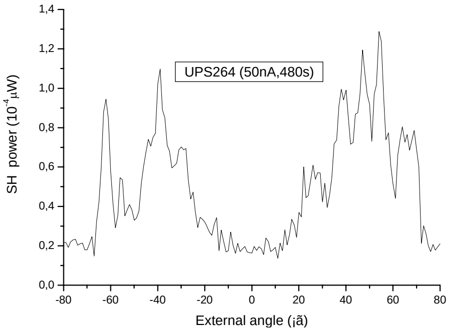

Fig. 1. Maker fringes at #5 irradiated position. (d33=0.003 pm/V).

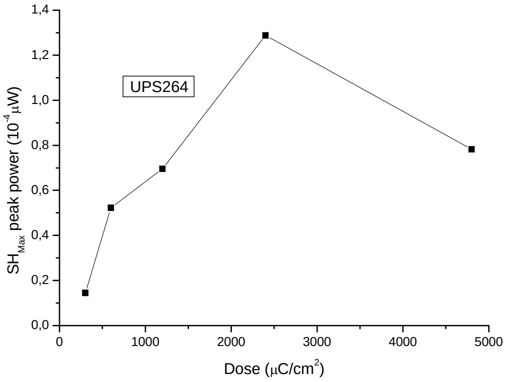

Fig. 2. SHG peak power versus electron doses.

3.2 Surface change

Using the interferometer microscope to observe the surface topography, it has been noted level differences between the irradiated and virgin regions as shown in Fig. 3 (after Ag film cleaning). The quantitative profile is plotted in Fig. 4. It was also observed that the surface change increased according to the increasing of the electron irradiating dose, which is shown in Fig. 5.

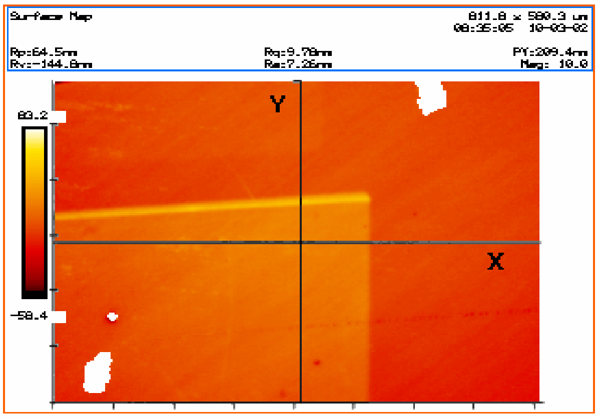

Fig. 3. The surface topography picture of the region #6 after Ag film cleaning. The line in yellow at the top is due to the beam sweeping mode.

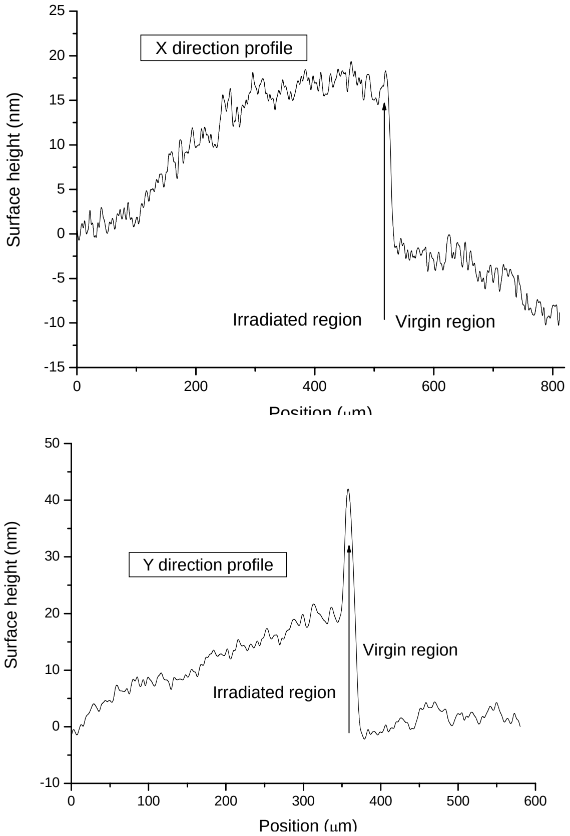

Fig. 4. Height profiles in the X and Y directions of sample N:H:SiO$_2$ films.

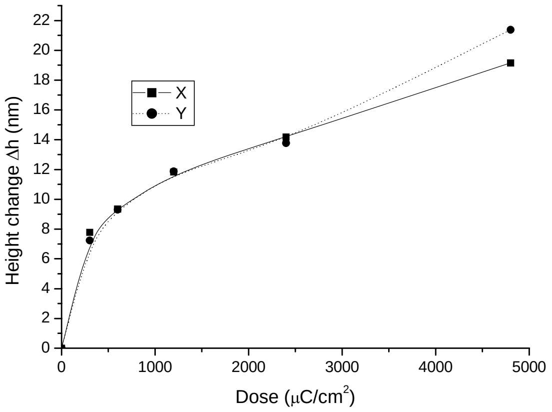

Fig. 5. The height changes in the X and Y directions according to different doses.

4. Discussion

The surface level change, we detect here, is positive. We have observed, on one hand, the same phenomenon for films of different composition (H:Ge:SiO$_2$ films) elaborated by MDECR but also on PECVD films poled thermally. In this last case, the film was in contact directly with the electrode and the surface level shift was positive whatever the polarity of the electrode. Our conclusion was that the change of volume is a surface effect related to charge injection. In the present case of electron beam poling, we have implanted electrons under an acceleration voltage of 25 keV. This corresponds to a depth of a few microns. There is thus a negative charge in the depth, which is balanced by a positive charge located at the surface. This charge is produced either by secondary electron emission or by trapping of positive charge from the air or also by releasing charges. The final surface charge leads to surface expansion as in the case of thermal poling experiment, we described before. It is worth noticing that the order of magnitude of the surface shift is the same in poling by electron-beam or thermal process.

On the other hand, we can observe in Fig. 4 that the largest level change is in the vicinity of the border of the irradiated region. This can be easily explained if we consider that the surface charges are mobile in the irradiated region and repulse each other.

After electron poling on samples, we have observed second harmonic generation. When the poled samples were heated in the Ar air, it was observed that the surface level changed again. Fig. 6 shows the film surface level changes (#5 irradiated region) due to different heating temperature. It is seen from the figure that the surface level change increases firstly and gets the maximum change at the 300°C temperature, and then decreases when the temperature increases. The surface is recovered at the temperature of 1250 °C, which means that there is no matter loss according to electron writing on the sample. Because the final surface charges induced by electron-beam poling are mobile in the irradiated region and repulse each other, they will absorb some energy and become more mobile and move strongly when the irradiated film is heated, so the height change becomes larger. But if the temperature is higher, some surface charges will absorb enough energy to release from the surface. So it is observed a maximum height change when the temperature is 300 °C. When we heat the sample at higher temperature, more surface charges will release from the surface till the film surface was recovered when the temperature is 1250 °C.

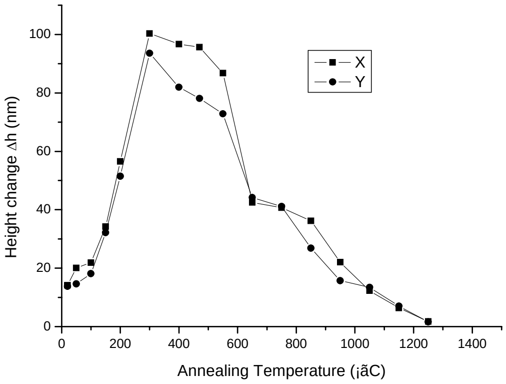

Fig. 6. The height changes in the X and Y directions according to different annealing temperatures (30 min annealing time) in #5 irradiated position: 50 nA and 8 min.

Normally, in thermally poled silica, the SHG possesses an excellent long term stability at room temperature, but if the thermally poled silica is annealed above room temperature, the SHG starts to decay with time. In order to investigate the stability of SHG in the N:H:SiO_2 vitreous films, we heated the films with different annealing temperatures and measured the SHG Maker fringes. The samples were isochromally annealed from 50 °C to 600 °C for half an hour and then were cooled to room temperature to measure the SHG each time. Fig. 7 shows the change of SH power in the N:H:SiO_2 films versus different annealing temperatures for 1/2h. It was indicated that the SH signal decreased to zero in trend when the annealing temperature was increased, and the oscillation was due to the unstable measurements in the Maker Fringe set-up or the measured position was different for each time.

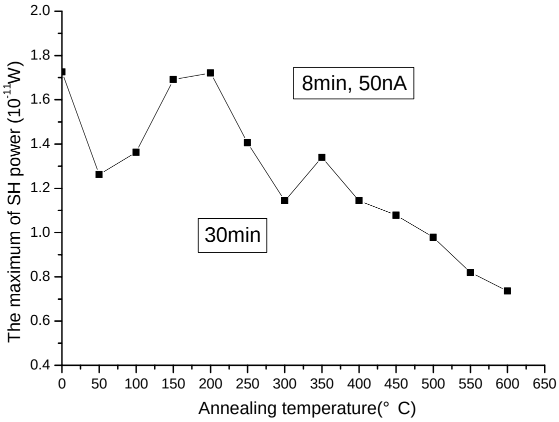

Fig. 7. The SH signal versus different annealing temperatures (30 min annealing time) in #5 irradiated position: 50 nA and 8 min.

It is well known [8] that there are mainly three kinds of paramagnetic defects in silica glass, E' center (≡Si·Si≡), nonbridging oxygen hole center (NBOHC: ≡Si-O·) and peroxy radical (PR:≡Si-O-O). EPR measurements shows that only GeE' and Ge(1) are detected [9]. When electron-beam irradiates the film, these defects trap some electrons. On the other hand, during the electron-beam irradiating, the incident electrons with some energy collide with electrons of outside the atomic nucleus and stimulate them to the empty energy levels or break away from the atomic nucleus and become the secondary electrons. In the same time, the incident electrons will become absorbed electrons after they have lost energy at last. So the positive charge centers are formed according to the emission of the secondary electrons. And the negative charge centers are formed due to the absorbed electrons. The inside electrostatic field is localized in these centers in between when these two oppositively charged centers exist side by side. A space-charge electrostatic field directing perpendicularly to the film surface is formed, which aligns the polar covalent bonds, for example Si-O in the film and breaks the symmetry of the film. So one new ministructure with the alignment of polar covalent bonds in the film is formed, which induces SHG. The magnitude of the induced nonlinear coefficient is in the order of 0.003 pm/V but the striking feature is the observation of surface level shift connected to poling. The weakness of the effect in some of the investigated films can be due to several properties of the material: one is the lack of efficient trapping, another one is the residual conductivity. Firstly the electric field cannot be created, in the second case, it cannot be maintained. They are three conditions to satisfy for obtaining a large $\chi^{(2)}$: a large $\chi^{(3)}$; a residual conductivity either electronic or ionic as small as possible, a large thermal stability of the trapped electrons. The $\chi^{(3)}$ condition is expected with hydroxyl species or with Ge in our case. $\chi^{(3)}$ could be even higher with heavy metal but conductivity and trapping efficiency would be problematic then.

When the electron-beam irradiated MDECR N:H:SiO_2 vitreous films were isochronous annealed, and the SH signal decreased till zero in the stability experiments finally. The stability of $\chi^{(2)}$ is expected to depend on glass material. Although in silicate glasses, the maximum level of $\chi^{(2)}$ does not depend much on glass chemical composition, the type of mobile ion and the glass host influence the dynamics of formation of $\chi^{(2)}$. In a similar way, the decay of $\chi^{(2)}$ is related to the poling mechanism itself which relies on migration of ions and subsequent freezing of the space charge field. In the electron-beam irradiated MDECR N-doped SiO_2 vitreous films, the ions are very few, so we can say that the decay of $\chi^{(2)}$ in these films is strongly related to the decay of frozen-in electric field induced by electron-beam irradiation. As a result of thermal annealing, not only the frozen-in electric field strength decays due to the thermally activated charge recombination but its spatial distribution is likely to change, which are both due to the thermally activated charges in the poled regions. So the $\chi^{(2)}$ profile is a function of the annealing time if the annealing temperature is certain, or a function of the annealing temperature if the annealing time is certain. When MDECR N-doped SiO_2 vitreous films were annealed isochromally, the space charges induced by electron-beam irradiation and charge centers formed during electron-beam irradiating will absorb some energy and become activated charges, and then they will move when they get enough energy, once the positive and negative activated space charges or charge centers meet together, the frozen-in electric field strength will begin to decay, so the $\chi^{(2)}$ starts to decay. Finally, more and more space charges and charge centers that own different charges meet together till the electric field is erased, the $\chi^{(2)}$ in the electron-beam irradiated MDECR N-doped SiO_2 vitreous films will decay to zero, the results of our stability experiments approved these and was shown in Fig. 7. On the other hand, the films were achieved with large H content because $\chi^{(2)}$ is also proportional to $\chi^{(3)}$ and it is known that H increases the hyperpolarisability. But water molecules because they are mobile, are detrimental of the stability. This is not the case for (Ge, Si)OH linkages.

5. Conclusions

We have demonstrated electron-beam poling in H: N:SiO_2 glass films elaborated by a variant of PECVD. The maximum magnitude of the induced second order nonlinear coefficient is in the order of 0.003 pm/V. The surface level shift due to electron-beam poling was observed with interferometer microscope and increased with the increasing of electron doses. It was found that the surface level shift was related to the implanted electron-beam dose but not to the induced second order nonlinear coefficient. The surface showed its maximum change when the film was heated at the temperature of 300 °C and was recovered at the temperature of 1250 °C, which meant that electron-beam writing did not lead matter loss in the films, but the SH signal decreased to zero in trend when the annealing temperature increased.

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