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Preparation of silver Nano-Crystal patterns in oxide glasses under electric field accompanied by heat treatment

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Nano-crystals embedded in glass always have interesting quantum effects, while nano-crystal patterns may have wide potential applications in preparing PIC, OEIC and other types of electronic and optoelectronic devices. A direct current electric field, accompanied by heat treatment, was applied on tellurite or silicate glass sheets. The silver ions in a diffused film were introduced into the glass matrix under a high-voltage electric field, instead of supplied during glass melting. The direct diffusion of metal ions, the nucleation and crystallization of nano-crystals in the glass were well controlled by the electric field accompanied by heat treatment. It was found that silver nano-crystal patterns can be transfer printed into tellurite and silicate glass sheets with both patterned diffusion and patterned crystallization.

Key words: Nano-crystal, Pattern, Glass, Electric field, Transfer print.

Introduction

Nano-crystal embedded glasses have many exciting optical properties such as luminescence and nonlinear optical performance [1-5], which are much better than a glass matrix and crystals by themselves. When the nano-crystals embedded in the glass substrate are arranged in the desired patterns, the nano-crystal patterns will have a potential application in photonic integrated circuits (PIC), optoelectronic integrated circuits (OEIC) and other types of optoelectronic devices. Nowadays, a variety of nano-pattern processes, such as electron beam lithography, X-ray lithography, extreme ultra violet lithography and nano-imprint lithography, have already been used in producing IC chips [6-9]. The types of nano-patterns with 100 nm in line width and less, can be prepared by these processes, but it is still difficult to prepare IC or OEIC chips with nano-crystal patterns. So, it is useful to find a new process to prepare nano-crystal patterns in glass substrates.

Nano-crystal embedded glasses can be prepared by a heat treatment process, a porous glass process, sol-gel methods, an ion exchange process etc. [10-12]. Some external fields, such as electric, magnetic and optic fields were also reported to be applied to control the nucleation and crystallization of nano-crystals [13-15]. It is important to control the growth of nano-crystals in the desired local areas when preparing nano-crystal patterns in glass substrates. Two methods can be adopted to control the patterned distribution of nano-crystals in a glass substrate, one is to control nucleation and crystallization of the glass in a local area under a DC electric field [16], the other is to only introduce precursive metal ions into the desired areas of the glass substrate and then separate nano-crystals in these areas. In this study, a heat treatment process accompanied by a DC electric field was reported to both local-area implant precursive metal ions into glass substrates and control the nucleation and crystallization of nano-crystal patterns in tellurite and silicate glass sheets.

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Experimental

The TeO_2-Nb_2O_5-BaO glasses were prepared using optical grade materials. Optical grade AgCl was introduced additionally from 0 to 4 wt%. The well-mixed batches of crystalline materials were melted at 750-850 °C for 10-20 minutes in a gold crucible. The melt was cast on to a steel plate and annealed at 250-300 °C for 2 h, and then cooled slowly to room temperature in the furnace. The glass samples were cut to a size of 20 mm × 20 mm × 1.5 mm and then polished. Also, commercial silicate microscope slides with a thickness of 1-1.2 mm were also used in the experiments.

A patterned silver film was printed onto the glass sheets using BYJ0775 silver paste, or was prepared by magnetron sputtering. The glass sheet was processed in a heat treatment apparatus accompanied by an auxiliary electric field, which is shown schematically in Fig. 1. The glass sheets were heat treated at 80-450 °C for 10-120 minutes, while a Au electrode was used to load the DC electric field with 200-700 V/mm at the same time.

The transmittance of pattern transfer-printed glass sheets was studied by CRT760 UV-VIS spectrophotometer. The nano-crystals embedded in the glass were observed by a Quanta 200FEG Field Emission SEM.

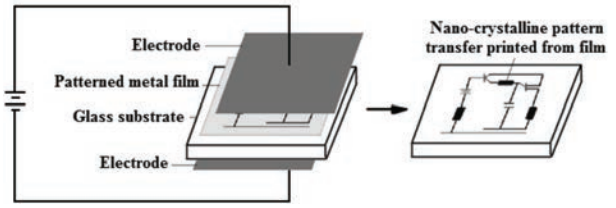

Fig. 1. A sketch diagram of nano-crystal pattern transfer printing.

Results and Discussion

Introduction of Ag^+ ions into glass substrates

Before silver nano-crystals were formed in the glass substrates, Ag^+ ions must be introduced into glass as precursive ions of silver nano-crystals. The Ag^+ ions can be introduced into glass substrates when melting the glass, and they can also be introduced by ion exchanging or ion implanting after melting. It was found that the Ag^+ ions can be introduced into glass sheet driven by a local-area applied external field [16], this makes it possible to obtain the nano-crystals in the desired local areas and form nano-crystal patterns in the glass sheet.

The Ag^+ ions can be introduced by diffusing into glass sheets under a DC electric field. When the silver film was coated on the surface of glass sheet, the Ag^+ ions in the film will diffuse into the glass sheet driven by the concentration gradient between the silver film and the glass substrate. The thermal diffusion of Ag^+ ions will also exist in the glass in a random way. When a DC electric field is applied onto the glass sheet, the diffusion driven by the electric field induces Ag^+ ions diffusing into the glass sheet along the electric field line.

Therefore, the diffusion of Ag^+ ions under an electric field includes random thermal diffusion, concentration gradient diffusion and highly directed electric field induced diffusion. If the treatment temperature of the glass sheet is uniform, the thermal diffusion can be neglected. So, the diffusion force of Ag^+ ions into glass sheet includes the force from the electric field F_E and the force from the concentration gradient F_C:

$$F_E = qE \tag{1}$$

$$F_C = KT\frac{\partial \ln \gamma}{\ln x} \tag{2}$$

where q is the quantity of diffusing ions, E is the intensity of the electric field, T is the treatment temperature, K is Boltzmann's constant, γ is the activity coefficient, and x is the diffusion distance.

According to Fick's first law, the diffusion flux of metal ions in the x direction, which is perpendicular to the glass sheet, J is:

$$J = -D\frac{\partial C}{\partial x} - D\frac{qEC}{KT} = -D_0 \cdot \left(\frac{\partial C}{\partial x} + \frac{qEC}{KT}\right) \cdot \exp\left(-\frac{Q}{RT}\right) \tag{3}$$

$$\text{So, } \frac{\partial C}{\partial t} = D \cdot \left(\frac{\partial^2 C}{\partial x^2} + \frac{qE}{KT}\frac{\partial C}{\partial x}\right)$$

$$= D_0 \cdot \left(\frac{\partial^2 C}{\partial x^2} + \frac{qE}{KT}\frac{\partial C}{\partial x}\right) \cdot \exp\left(-\frac{Q}{RT}\right) \tag{4}$$

where C is the content of metal ions, D is the diffusion coefficient, D_0 is the frequency factor, and Q is diffusion activation energy.

In addition to the structure and performance of the glass substrate and the separate crystals, the diffusion of metal ions is also affected by the electric field intensity, the concentration gradient, the treatment temperature and time. When the glass sheet is at a lower temperature, the diffusion of the metal ions is mainly controlled by the DC electric field, and the diffusion due to the concentration gradient is smaller. The ions will be implanted into the glass sheet mainly along the electric field line. When the treatment temperature is increased, the diffusion due to the concentration gradient will increase gradually, it will diffuse metal ions not only from the transfer printing film to glass substrate, but from metal-ion-containing areas to metal-ion-free areas, which results in nano-crystal patterns which are out of focus. Therefore, it is important to decrease treatment temperature as far as possible to restrain the concentration gradient induced diffusion, and increase the electric field induced diffusion.

If the Ag^+ ions were introduced when melting the glass, these ions occupy some positions in the glass network and are in a stable state. By contrast, when the Ag^+ ions are implanted under an electric field, the solidified glass structure is difficult to expand to accept new ions. Therefore, the implanted Ag^+ ions have to wedge into narrow interstitial positions in the glass network with a compressive stress. When the Ag^+-ion implanted glass is heat treated, the nucleating and crystallizing temperature of the nano-crystals will be decreased by the stress, and the size will also be decreased because of difficult Ag^+-ion diffusion in the dense glass structure.

FESEM patterns of silver nano-crystals in niobic tellurite glasses are shown in Fig. 2. When the 2% AgCl containing glass was annealed at 360 °C, which was already near its softening point, the average size of nano-particles in the glass was about 30 nm (Fig. 2a). When the Ag^+ ions were implanted by using an electric field, the crystallizing temperature was decreased to 320 °C, and the average size of nano-particles was also decreased to about 20 nm (Fig. 2b). The nano-particles retained their small size on the glass surface, even when the quantity of particles was much more than that in the cross section of Ag^+ implanted glass and AgCl containing glass (Fig. 2c).

Nucleation and crystallization of silver nano-crystals in the glass substrates

Glasses are a type of metastable materials which are stable dynamically but unstable thermodynamically. They will nucleate and then crystallize when the heat treatment provided can overcome the phase transition potential barrier. If an auxiliary DC electric field is applied to a glass sheet accompanied by heat treatment, the influence

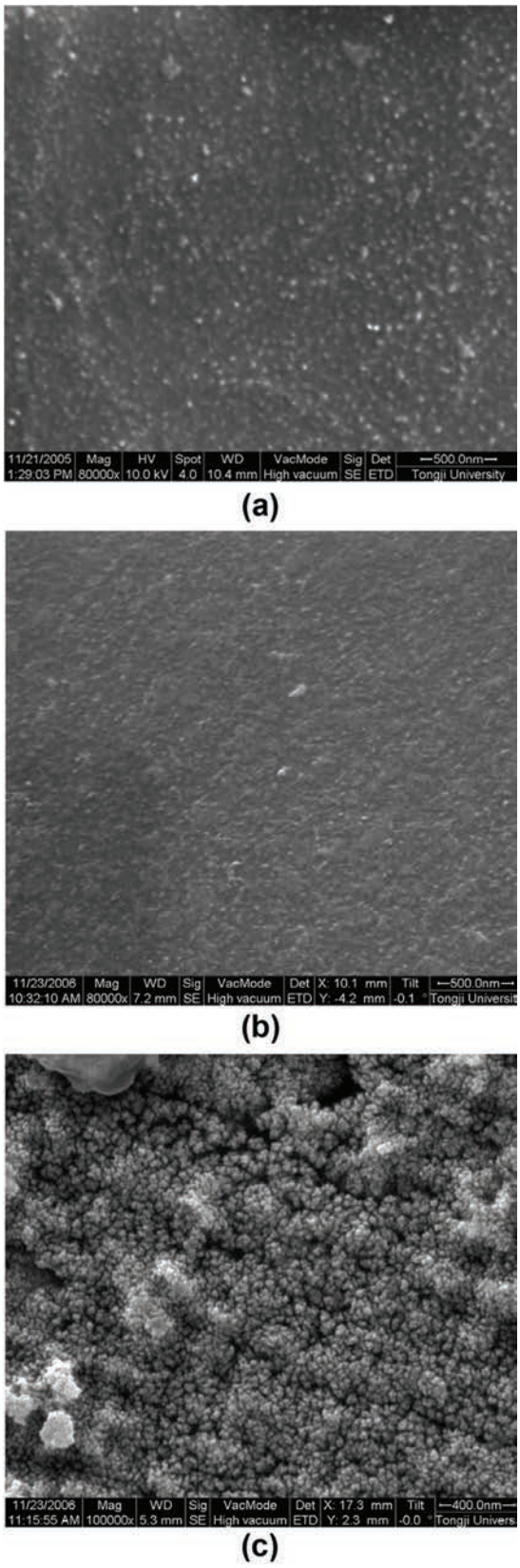

Fig. 2. The FESM patterns of silver nano-crystals in niobic tellurite glasses. (a) The section of AgCl-containing tellurite glass sheet after being annealed at 360 °C, (b) The section of tellurite glass after being diffused with Ag^+ ions at 340 °C under an electric field, (c) The surface of tellurite glass after being diffused with Ag^+ ions at 340 °C under an electric field.

of the electric field on the phase transformation of the glass must be considered. The free energy change ΔG of nucleation is seen as Eq. 5 [13]:

$$\Delta G = V\Delta G_V+\Delta G_S+\Delta G_E = \frac{4}{3}\pi r^3 \left[\Delta G_V-\frac{1}{2}(\varepsilon_2-\varepsilon_1)E^2\right]+4\pi r^2\sigma \quad (5)$$

where ΔG_V is the strain energy per unit volume, ΔG_S is the surface free energy change, and ΔG_E is the free energy change due to the electric field. r is the radius of a nucleus, σ is the effective surface free energy per unit area. ε_1 and ε_2 are the dielectric constants of the glass and crystals, E is the intensity of the electric field.

If the dielectric constant of the glass is less than that of the corresponding crystal, the auxiliary electric field will accelerate nucleation and crystallization of the glass. It will play a restraining effect otherwise [13].

Heat treatment is one of the most commonly used steps to stimulate growing nano-crystals from a glass. The silver nano-crystalline particles were separated out from the Ag^+ diffused niobic telluite glass sheet when heat treated at 310-360 °C. They could also be separated out from silicate microscopy slides when heat treated at 450-500 °C. The process of Ag^+ ions' diffusion and the silver nano-crystal particles' growth could be merged into one step when a treatment temperature is available. For example, the two processes occurred at the same time when the treating temperature of niobic tellurite glasses was from 310-360 °C. The crystallization temperature of silver nano-crystals in silicate glasses is always more than 450 °C, a better choice for these types of glasses was to diffuse Ag^+ ions at 300-350 °C at first, and then re-anneal at 450-500 °C to obtain nano-crystals.

The influence of treatment temperature on the transmittance of niobic tellurite glass sheets is shown in Fig. 3. The transmittance was decreased with an increase in the treatment temperature. When the temperature exceeded 270 °C, the plasma resonant absorption of silver nano-crystals appeared near 500 nm. It seemed that when the temperature was lower than 270 °C, the combined power of the heat treatment and electric field could only induce a few Ag^+ ions diffusing into the glass sheet. The combined power would begin to accelerate nucleation and crystallization of nano-crystals simultaneously when the temperature was greater than 270 °C. However, if the treatment temperature was too high, the glass will lose its transparence because of the large size of the separated crystals, and the plasma resonant absorption was also decreased from a drop of the quantum effects of the larger crystals. The tellurite glass will be broken down when the electric filed intensity exceeds 700 mm/V at 350 °C and higher.

The influence of electric field intensity on the transmittance of microscopy slides is also shown in Fig. 4. After the slides were implanted with Ag^+ ions under an electric field at 300 °C, they were re-annealed at 500 °C

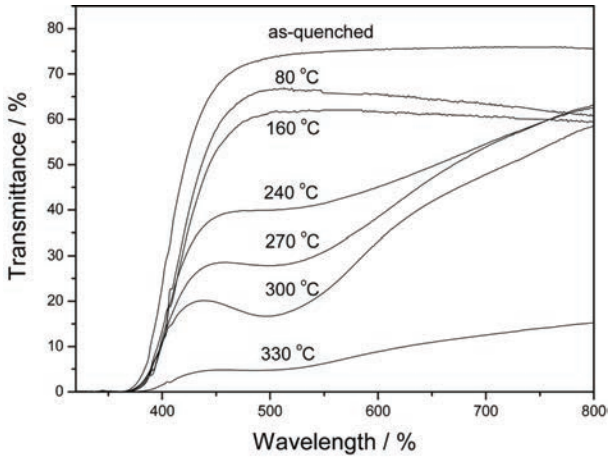

Fig. 3. Effect of treatment temperature on the transmittance of tellurite glass sheets under an electric field accompanied heat treatment of 350 V/mm.

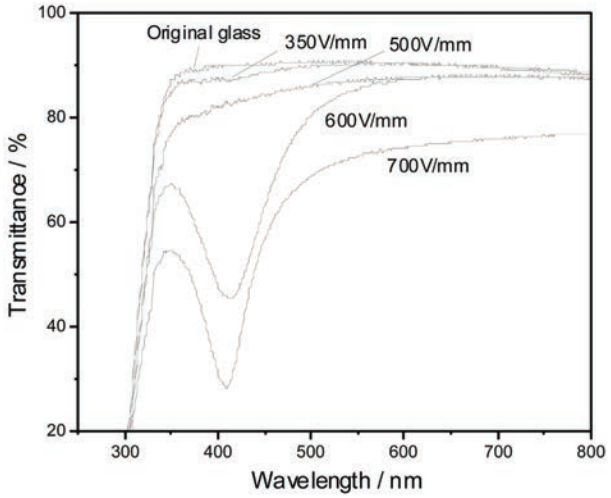

Fig. 4. Effect of electric field intensity on the transmittance of silicate glass slides under an electric field accompanied heat treatment at 300 °C

to form nano-crystal particles. If the electric field intensity was too low, it is difficult for Ag^+ ions to diffuse into the dense glass network structure. When the electric field was powerful enough, a large amount of Ag^+ ions entered the glass sheet along the electric field lines, and then silver nano-crystals were formed by the re-annealing process, the plasma resonant absorbing peak of silver nano-crystals can be seen apparently in Fig. 4.

Transfer printing silver nano-crystal patterns into glass substrates

If nano-crystal particles can be designed in desired patterns, they will have wide potential applications in such areas as manufacturing PIC, OEIC and some other optic or electronic devices.

The electric field has a high orientability, it can induce metal ions to diffuse into a glass substrate along the electric field lines and form nano-crystal particles in some definite areas. When the Ag^+ ion-containing glasses were heated at

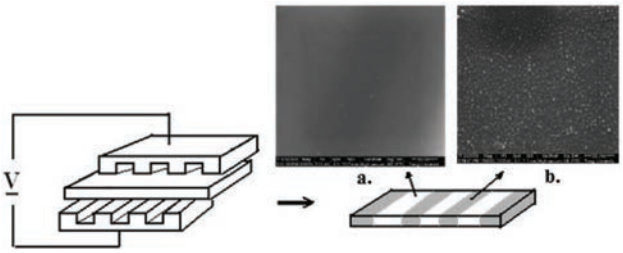

Fig. 5. A sketch of the heat treatment with a local area applied electric field and the FESEM patterns of niobic tellurite glass sheet.

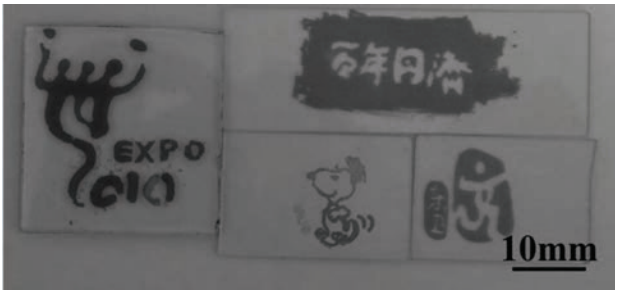

Fig. 6. Silver nano-crystal patterns in silicate glass slides.

a temperature little below its nucleating and crystallization region, the applied heat treatment conditions would not provide enough power to separate the crystals (as shown in area a of Fig. 5), while the local-area applied auxiliary electric field will provide the supplemental energy to separate nano-crystals (as shown in area b of Fig. 5).

When the electric field is used to implant metal ions into a glass substrate, if its intensity is powerful enough to let the ions diffuse into the glass, and the thermal diffusion and concentration gradient diffusion can be restrained as far as possible, the metal ions in the coated silver film pattern will diffuse into the glass sheet mainly along electric field lines, and then nano-crystal particles can be separated in some desired areas under an electric field accompanied by heat treatment.

Silver nano-crystal patterns are shown in Fig. 6. After coating with patterned silver paste on the surface of microscope slides, the Ag^+ ions were implanted into the glass sheet under a 200-400 V/mm electric field at 300-360 °C, and then re-annealed at 500 °C. A variety of silver nano-crystal patterns were transfer printed into glass slides. The patterns already penetrated into the glass slides to a depth of hundreds of micrometres, and thus the stability and wear resistance of these patterns were much better than those made by chemical deposition or physical deposition.

Conclusions

Preparation of silver nano-crystal embedded glasses includes introducing Ag^+ ions into the glass substrates and separating nano-crystals from the glass. Ag^+ ions can be implanted into glass sheets from a coated silver film under a DC electric field accompanied heat treatment. The electric field can also provide supplemental energy to control the

growth of nano-crystals accurately during heat treatment. When the heat treatment temperature is low enough to restrain the concentration gradient diffusion, the electric field induced diffusion will play an important role. The highly directed electric field makes it possible to well control the Ag^{+}-ion-diffusion mainly along the electric field line and then grow silver nano-crystals in desired local areas, thus the silver nano-crystal patterns can be clearly transfer printed into tellurite or silicate glasses sheets.

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