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Preparation of thick, crack-free germanosilicate glass films by polyvinylpyrrolidone and study of the UV-bleachable absorption band

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Abstract

With addition of polyvinylpyrrolidone (PVP) transparent, stable GeO_2–SiO_2 sols containing up to 60–80 mol% GeO_2 were synthesized using tetraethyl orthogermanate (TEOG) and tetraethylorthosilicate (TEOS) as precursors for germania and silica, respectively. It was shown by TEM analyses that the PVP can be absorbed onto the colloidal particles providing steric hindrance for the combination and aggregation of particles. These sols were observed showing rapid increase in viscosity within both the early period and the end period of sol aging time, but exhibiting a viscosity value of about 28 mPa s within the rest aging time (45–90 h) satisfying well the requirements for the deposition of thick films by cycles of dip-coating operation. It was determined by TG-DTA and SEM analyses that the densification of GeO_2–SiO_2 gel material with PVP was much more retarded than the gel without PVP resulting in crack-free germansilicate films with a thickness of 3 μm. The crystallization behavior of germansilicate films was enhanced with the increase of GeO_2 content but glass films with a composition of $60GeO_2 \cdot 40SiO_2$ was obtained by sintered at 700 °C for 1 h and annealed at 550 °C under a flowing H_2/N_2 atmosphere for 2 h. FT-IR analyse showed that the heat treatment at 700 °C for 60 min was effective to remove the organics and hydroxyl groups in the germansilicate film. An intense 5 eV absorption band was distinctly observed in films. The intensity of this absorption band was found to be effectively bleached by UV illumination. Weak photoluminescence emission bands which originated from the neutral oxygen di-vacancy (NODV) were detected near 375 and 276 nm. Therefore, the 5 eV absorption band observed in this work was mainly caused by the neutral oxygen monovacancy (NOMV). A saturated absorptivity change of the UV-bleachable band after prolonged illumination was found to be $256\ cm^{-1}$ for the $60GeO_2 \cdot 40SiO_2$ films implying the NOMV concentration in the films reached about $3.8 \times 10^{18}\ cm^{-3}$.

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1. Introduction

It is well known that there is an UV absorption band near 5 eV for germanosilicate material and that this absorption band is associated with an oxygen-deficient defect [1,2]. The 5 eV absorption band of germania-related oxygen-deficient defects is responsible for the photosensitivity of germanium oxide based materials [3,4]. This makes it possible to manufacture new integrated optical components using the photorefractive index changes such as Bragg grating inscriptions and UV direct patterning of waveguides by light near 5 eV or at longer wavelengths by means of two-photo absorption [5].

It is reported that the 5 eV absorption band is composed of two components: the absorption band centered at 5.06 eV formed by a neutral oxygen monovacancy (NOMV) such as Ge–Ge or Ge–Si bonds and the absorption band centered at 5.16 eV formed by a neutral oxygen di-vacancy (NODV), i.e., Ge^{2+} coordinated by two oxygens, respectively, [6,7]. Only the absorption band at

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5.06 eV of NOMV is photobleachable due to the conversion of NOMV to a Ge E′ center to form the intense absorption band above 5 eV by illumination with 5 eV light. These UV absorptions contribute to permanent increase in the refractive index of the glasses that can be used in the fabrication of gratings [8]. Therefore, the synthesis of GeO_2 based materials with a higher concentration of the photobleachable NOMV is desirable for efficient design of grating devices.

Various methods including melting, flame hydrolysis, vapor axial deposition(VAD), sputtering deposition, chemical vapor deposition (CVD), ion implantation and sol–gel have been employed to fabricate GeO_2 based optical materials [9–14]. Compared with other methods, sol–gel technology provides a very simple route to the preparation of thin films on simple- or complex-shaped substrates at low temperature and low cost [15–20]. This makes it possible to fabricate modern integrated optical components which have complicate structures and shapes, for example, hollow-core fibers, concavo-convex cavity waveguides, etc. It was confirmed by our previous research that thick sol–gel oxide films could be conveniently deposited inside a capillary tube with a diameter of 500 μm via cycles of dip-coating operation [21].

Despite of its notable advantages, there are disadvantages in sol–gel process. It is well known that the cracks could be easily formed in the sol–gel materials. It has been reported by Kozuka et al. that the maximum thickness achievable without crack formation via non-repetitive deposition is often below 0.1 μm for non-silicate oxide films [22]. Thus, cycles of dip-coating operation are employed to prepare thick sol–gel films [23]. To do so, a coating solution with long gelation time is needed. However, sols are generally prepared via a hydrolysis and polycondensation reaction of alkoxides, and hence show an increase in viscosity with time. Because the thickness of the films increases with sol viscosity, sols showing a rapid increase in viscosity cannot be used as a practicable coating solution for the preparation of thick films [24].

It is believed that the higher concentration of the NOMV can be made by higher germanium oxide content or heat treatment under reduced atmosphere. Niahii et al. have prepared a 4.6-μm-thick germanosilicate film containing up to 50 mol% germanium oxide by sputtering deposition method, and an intense absorption band at around 5 eV was distinctly observed [25]. However, the work concerning thick sol–gel germanosilicate films with high GeO_2 content is virtually very limited because germanium alkoxides, such as germanium ethoxide et al., are extremely moisture sensitive leading to the formation of a sol with very short gelation time. Although the germanosilicate films containing up to 45 mol% germanium oxide were fabricated by sol–gel method but the film thickness was usually lower than 1 μm [10,12]. Pure GeO_2 films were synthesized by Jae Hyeok Jang et al. using sol–gel spin-coating method, but the film thickness is only about 390 nm and this method cannot be used to deposit oxide films on substrates with complicate shapes [26]. Another problem concerning the preparation of thick germanosilicate films containing a high GeO_2 content is that these materials undergo easily crystallization during calcination and but glass is generally a suitable waveguide material because glasses without scattering sources are highly transparent in visible and IR wavelength regions [26,27]. Therefore, techniques suppressing the increase in sol viscosity, the cracks and crystallization in thick sol–gel germanosilicate films with high GeO_2 content are in great demand.

In recent years, polyvinylpyrrolidone (PVP) has been used to synthesize thick, crack-free $BaTiO_3$ films [22–24]. In this work, we attempted to improve the stability of SiO_2–GeO_2 sols with high GeO_2 content and suppress the cracking in the sol–gel film materials by adding PVP. Undoubtedly, the addition of PVP will has negative effects on the preparation of GeO_2 based materials, for example, a heat treatment at high temperature for long time is needed to remove the PVP bringing difficulty to obtain glass films. By optimizing the addition amount of PVP, the composition of SiO_2–GeO_2 sol and heat treatment conditions, thick (3 μm), crack-free germanosilicate glass films containing up to 60% GeO_2 was obtained. The films were annealed under reduced atmosphere and subjected to UV illumination for the investigation of UV-bleachable absorption band.

2. Experimental

Tetraethyl orthogermanate (TEOG), tetraethylorthosilicate (TEOS), and polyvinylpyrrolidone (PVP, average molecular weight 630 000) were used as starting raw materials. Initially, PVP was sufficiently mixed with TEOG and TEOS in ethanol, respectively. TEOS was pre-hydrolyzed with H_2O and HCl addition for 1.5 h at room temperature under continuous stirring in a glass beaker followed by adding the PVP-TEOG-ethanol solution. The ethanol aqueous solution was then gradually added into the glass beaker with stirring followed by further stirring for several hours to let the TEOG and TEOS hydrolyze sufficiently at room temperature. The following molar ratios were used; TEOS:ethanol:H_2O:HCl = 1:30:2:0.03, TEOG:ethanol:water = 1:30:4, TEOS:TEOG = 0:100–90:10. For comparison, GeO_2–SiO_2 sols without PVP were also synthesized according to the preparation sequences described above.

Sol–gel GeO_2–SiO_2 films were deposited onto silica glass substrate using cycles of dip-coating method. Each substrate was immersed into the sol reservoir and allowed to soak for 30 s. The coated substrate was then removed from the bath at controlled rates ranging from 3 to 15 cm/min. Following the deposition of each layer, the samples were held nearly vertical in a clean cabinet and dried at 80 °C. Subsequent layers were deposited directly on the dried gel and the multilayered samples were sintered at 700 °C in O_2 atmosphere for 60 min. Then the samples were subjected to thermal treatment at 550 °C under a flowing H_2/N_2 (1:20 volume ratio) atmosphere for 120 min. The temperature was increased or decreased at a rate of