NOVEL FABRICATION TECHNIQUE FOR ANTIREFLECTION MICRO-STRUCTURES USING FLUORINE-DOPED SiO_2 FILMS

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Abstract Two-dimensional cone-shaped periodic structures with 1μm period were fabricated by a dry and wet etching of a fluorine-doped SiO_2 film. The fluorine content in the film was adjusted in order to control the etching rate of the film. The Fresnel reflection of silica plate was reduced from 3.5% to 0.7% by the formation of this microstructure. Surface morphology became drastically smooth by the overcoating of a SiO_2 thin layer after the wet etching without increasing the reflection.

1. Introduction

Surface-relief gratings with a period smaller than the wavelength of light have been studied extensively as new diffractive optical elements. Especially a two-dimensional (2-D) sub-wavelength structure (SWS) was received much attention because of its antireflection (AR) effect in a wide wavelength region and a wide incident angle of input light. Theoretical and experimental studies of such structures were carried out vigorously for the development of advanced optical elements [1–8]. In most previous reports, SWS surfaces of a resist were fabricated by a two-beam interference method [1, 2] or the combination of a resist lithography and a reactive ion etching (RIE) [3–5]. In order to attain the lowest reflection, the precise control of each groove profile is required. These methods, however, are undesirable for the formation of such restricted profile. In this paper, a novel fabrication technique of a cone-shaped micro-structure on a SiO_2 glass surface was demonstrated, in which a fluorine-doped SiO_2 film and its patterning by combination of dry and wet etchings were used. Fluorine content in the film was changed gradually in the direction of film thickness. We successfully prepared a 2-D array of corn-shaped micro-structures with low reflectance upon a SiO_2 substrate.

2. Fabrication

A plasma enhanced chemical vapor deposition (PECVD) with parallel-plate electrodes was used for the preparation of fluorine-doped SiO_2 films. $Si(OC_2H_5)_4$ liquid was vaporized at 80ºC and mixed with CF_4 gas. These raw materials were decomposed in an O_2 plasma, and then deposited on the substrate. $Si(OC_2H_5)_4$ and O_2 flow rate were 7 and 233 sccm, respectively. An operating pressure, a substrate temperature, and a RF power were 0.4Torr, 400ºC, and 250W, respectively. Fluorine content in the films was controlled by changing a CF_4 flow rate. The F_2 content was almost proportional to the CF_4 flow rate, which could be increased up to 60sccm. The films became optically inhomogeneous when the CF_4 flow rate was higher than 70sccm.

Figure 1 shows the dependence of etching rate on F_2 content in fluorine-doped SiO_2 films. The concentration of F_2 in the film was estimated by XPS. The films were etched in a 5%-diluted HF solution at 25ºC. The etching rate increases drastically in the region of F_2 content exceeded 4mol%. The etching rate of the film containing 9mol% F_2 is 8 times as rapid as the value of the pure SiO_2 film.

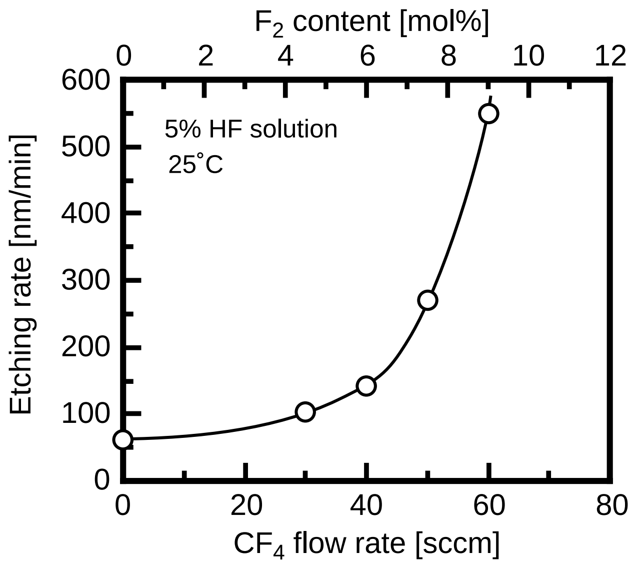


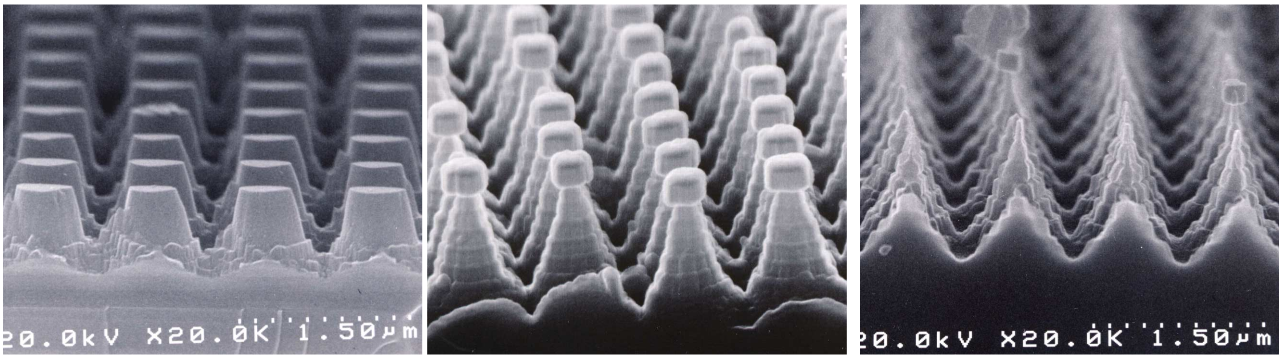
Fig. 1 Etching rate versus CF_4 flow rate for fluorine-doped SiO_2 films

2-D periodic micro-structures were fabricated upon a fluorine-doped SiO_2 film with six layers deposited on a SiO_2 or Si substrate, in which the thickness of each layer was 0.2μm. The F_2 contents in each layer were 0, 6, 7, 8, 9, and 0 mol%, respectively, from the substrate. A photoresist of 1μm thickness was coated on the surface of the film, and exposed it twice to an interference beam of a 325nm-wavelength He-Cd laser light. Between the two-irradiation steps, the substrate was rotated by 90º. As a result, a 2-D periodic holed pattern with 1μm period was obtained. A Cr film of 0.2μm thickness was coated on the patterned photoresist by a DC sputtering. After removing the photoresist, a 2-D dotted Cr mask was remained on the surface. The films were etched vertically by an inductive-coupled plasma RIE (ICP-RIE) using CHF_3 gas, followed by a wet etching using a 5%-diluted HF solution for 25s at 25ºC.

Figure 2(a), 2(b), and 2(c) show the cross-sectional structures before, under, and after the wet etching, respectively. A corn-shaped 2-D micro-structure was obtained after the wet etching of the cylindrical structure. The final depth of the grooves was ~1μm. The Cr mask and pure-SiO_2 top layer were removed at the final stage of the wet etching. The SiO_2 top layer enabled the formation of a sharp tip at the top of cone-shaped micro-structures.

3. Characterization and Discussion

Figure 3 shows a transmittance spectrum of the 1-mm-thick SiO_2 plate having the micro-structure on a side. The bottom surface of the plate is optically flat. The incident light was randomly polarized and perpendicular to the micro-structure surface. Under perpendicular incident light, a Fresnel reflection of 3.5% is expected at one surface of a flat silica substrate. Therefore, the maximum theoretical transmittance is 96.5 % when one face of the SiO_2 plate is perfectly antireflective.



(a) before wet-etching (b) under wet-etching (c) after wet-etching

Fig. 2 SEM photographs of the fabricated structures

As shown in Fig. 3, the transmittance of the sample with a 2-D cone array was much better than that of the silica plate at ≥ 1.35μm in wavelength. The drastic decrease in transmittance at ≤ 1.35μm is probably due to the diffraction into the substrate. A small dip at around 2.2 μm and the decrease at ≥ 2.65μm in transmittance are owing to the absorption by OH impurities in the substrate [9]. We obtained the transmittance with little wavelength-dependence at wavelengths from 1.4μm to 2.4μm. A maximum transmittance of 95.8% was obtained at 1.85μm. The reflectance due to the cone-shaped micro-structure was estimated as 0.7%, which is one-fifth of the 3.5%-Fresnel reflection at a SiO_2 flat surface. Although a transmittance of the sample before the wet etching was also better than the untreated SiO_2 substrate, it was significantly dependent on the wavelength as shown in Fig. 3. AR effect of the fabricated structure was calculated by use of a rigorous coupled-wave analysis (RCWA) [10, 11]. In this calculation, a 2-D array model with a five-level pyramidal profile was used for simplification. The structure used in the calculation has grooves with 1μm depth and 1μm period. The refractive indices of each layer are 1.46, 1.45, 1.44, 1.43, and 1.42, respectively, from the substrate. The calculated transmittance spectrum is shown by a dotted curve in Fig. 3. The maximum transmittance and the minimum reflectance were estimated as 96.49% and 0.0095% at 1.32μm, respectively, which were better than the experimental results. The discrepancy indicates that the reflectance should be decreased more by the improvement of

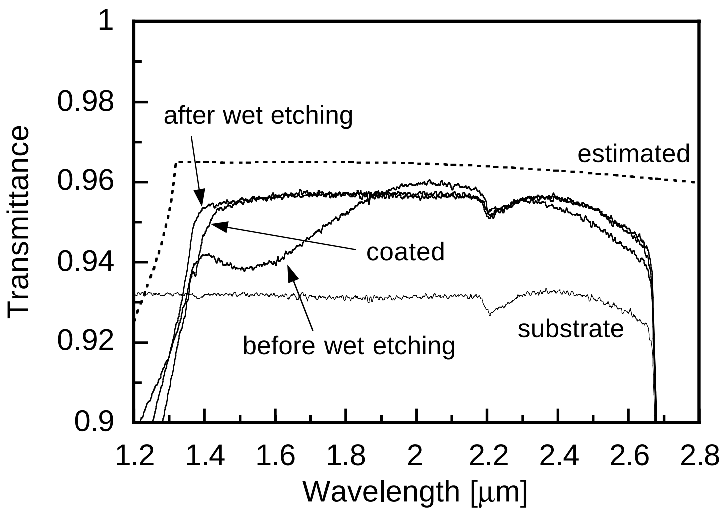


Fig. 3 Transmittance spectra of 1-mm-thick SiO_2 samples. The spectrum of a SiO_2 substrate with flat surfaces is also shown for comparison. The dotted curve shows the theoretically estimated spectrum of the SWS surface after wet etching.

the optical homogeneity of the micro-structure.

Formation of replicas on other materials is important to reduce the fabrication cost. The fabricated micro-structure surface, however, might be unsuitable for a master because of the roughness in each cone-shape structure, as shown in Fig. 2(c). Then a SiO_2 thin layer of 1μm in thickness was over coated on it by PECVD. Figure 4 shows the surface morphology of the overcoated micro-structure, whose transmittance spectrum is also shown in Fig. 3. The spectrum is very similar to that before the overcoating. The preparation of replicas using this coated micro-structure should be reported in the near future.

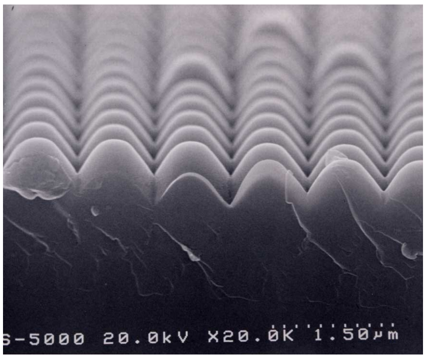


Fig. 4 SEM photograph of the coated micro-structure

4. Conclusion

We have proposed and demonstrated a novel fabrication technique of 2-D micro-structure array for AR silica surface. A cone-shaped micro-structure could be easily fabricated upon a fluorine-doped SiO_2 glass using by a conventional photolithography followed by the wet etching with a HF solution, because the rate of the wet etching was strongly depended on the content of fluorine. An anisotropic etching method was easily performed by controlling the amount of fluorine in SiO_2. We attained the lowest reflectance of 0.7% at 1.85μm in wavelength, which was about one-fifth of a flat SiO_2 surface. The surface morphology of the micro-structure after etching was drastically improved by overcoating with a SiO_2 thin film. Further works are continued in order to fabricated the confirmed micro-structures having deeper grooves, shorter period, and so on, which is expected to show an excellent AR effect in shorter wavelength range.

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