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Application of flowable oxides in photonics

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Polymer hydrogen silsesquioxane (HSQ) solution in methyl isobutyl ketone (MIBK) commercially known as FOx (flowable oxide) is an alternative material to silicon dioxide obtained by chemical deposition. Standard process to obtain amorphous SiO_2 film from polymer HSQ includes: deposition by spin coating, removal of solvent by softbake on hotplate and oxidation of materials by heating in an oven or oxygen plasma treatment. Having parameters similar to those of SiO_2, polymer HSQ after softbake is sensitive to an electron beam and also to wavelengths below $\lambda = 157$ nm. Due to those factors, it can be used as a high resolution (20 nm details) negative mask in next generation lithography and in e-beam lithography. Removal of FOx after hardbake is possible only with dry etching or in HF solution. The paper reports on possibilities of application of HSQ polymer for integrated optoelectronics. Technology of obtaining an SiO_2 layer from HSQ polymer is described. Measurements of thickness, refractive index and transmittance from 200 nm to 800 nm are reported for the fabricated layers.

Key words: *hydrogen silsesquioxane; polymer HSQ; flowable oxide photonics*

1. Introduction

Integrated optics is one of the most rapidly growing areas of science. The material base for optoelectronics devices and photonics structures is still growing. New methods for fabrication of optoelectronic structures or modification of existing ones are continuously created, and new materials are used in those processes. One of the materials, polymer hydrogen silsesquioxane (HSQ), is especially promising in nanoengineering applications. Most popular use of HSQ is a high-resolution negative inorganic e-beam resist. Trellenkamp [1] reported 20 nm wide lines fabricated from HSQ using electron beam lithography. HSQ is sensitive to radiation below $\lambda = 157$ nm [2] and behaves like a negative photoresist for these wavelengths. However, due to low

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sensitivity, it has been considered useless for next generation lithographies (NGLs). On the other hand, this low sensitivity is related to high resolution capabilities of HSQ. Peuker [2] proposed use of "mix-and-match" combinations of e-beam lithography with NGLs. Another idea is to use HSQ in room temperature nanoimprint lithography. The pattern is transferred to suitably prepared HSQ polymer. According to Chen [3], details of size from micrometric scale down to sub 100 nm have been successfully fabricated. A possibility to replace PECVD SiO_2 used as a mask in dry etching process by HSQ amorphous silica has also been investigated. Lauvernier [4] applied HSQ as a mask in RIE technique on GaAs. The value of etching selectivity was compared to PECVD SiO_2 relative to GaAs. For HSQ polymer, selectivity varied from 3 to 7 depending on oxidation conditions. The best results were obtained for oxidation in oxygen plasma. Silicon dioxide fabricated by PECVD method exhibits etching selectivity to GaAs of about 7.

In this paper, results of our investigation of optical parameters of layers fabricated with HSQ polymer are presented. HSQ amorphous silica layers are compared to PECVD SiO_2 and thermal oxides.

2. Experimental

Silicon wafers were spin coated with FOx®-13 from DowCorning HSQ solution in methyl isobutyl ketone (MIBK). Surfaces were cleaned in butyl alcohol, acetone, isopropyl alcohol and baked at 200 °C for 30 minutes directly before coating. According to the producer, it is possible to achieve amorphous silicon dioxide of the thickness between 174 nm and 333 nm from FOx-13. The applied procedure consists in spin-coating of the material, solvent removal and densification by baking on a hot plate for 120 s at 150 °C and next for 120 s at 220 °C. The layers were transformed to amorphous silica by curing at 325 °C for 60 min. Their thicknesses and refractive indices were measured using a single wavelength ellipsometer EL-7 at $\lambda = 632.8$ nm. Standard deviation of the ellipsometer for thickness measurements is $\sigma_t = \pm 1.2$ nm, and for the refractive index $\sigma_n = \pm 0.006$. Transmittance was measured with a spectrophotometer Thermospectronic, UNICAM UV 300 at the wavelength range 200–800 nm. Beside measurements of HSQ layers, thermal silicon dioxide ($t = 200$ nm) and PECVD SiO_2 ($t = 128$ nm) were also measured.

3. Results

3.1. Thickness and refractive index

The samples were prepared at various rotational speeds to characterize the process of coating. Table 1 presents results of thickness measurements. Due to a high level of contamination of air in the laboratory, it was not possible to obtain high quality films at 1000 rpm. The best layers were obtained at 4000 rpm. (Fig. 1).

Table 1. Thicknesses of films obtained with various rotational speeds of a spin-coater

Np.	Rotational speed [rpm]	Thickness [nm]	Refractive index	Conditions
1	1000	–	1.386	*T* = 21 °C *H* = 36%
2	2000	242		
3	3000	200		
4	4000	162		
5	5000	150		
6	6000	138		

Fig. 1. Thin layers of spin-on dielectrics (HSQ polymer) coated at various rotational speeds: a) 1000 rpm, b) 2000 rpm, c) 3000 rpm, d) 4000 rpm, e) 5000 rpm

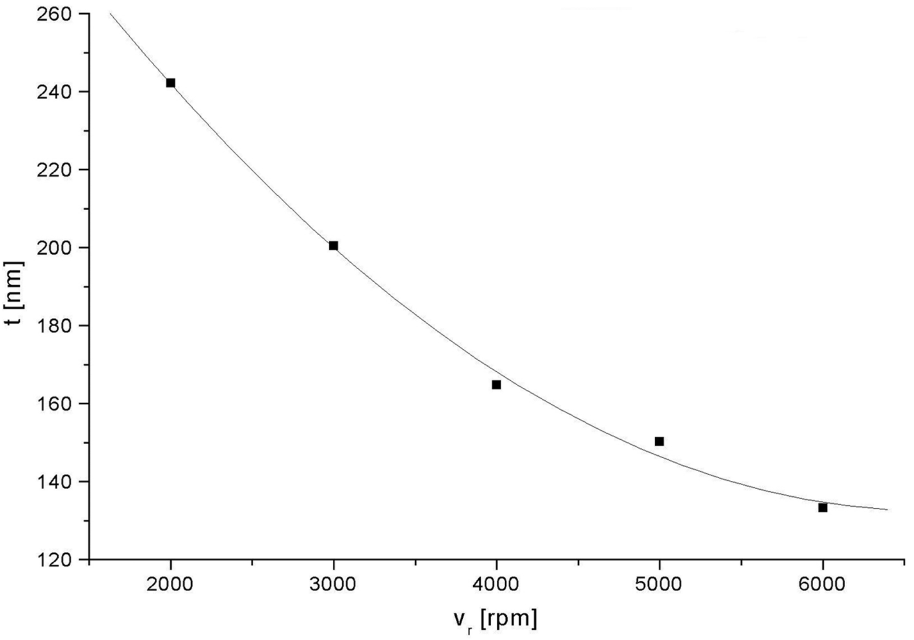

Fig. 2. Dependence of thickness of HSQ layers on the rotational speed of a spin-coater

The dependence of thickness on the rotational speed for fabricated layers is presented in Fig. 2. Parabolic type of dependence is typical of spinned material, being a result of faster solvent evaporation at higher rotational speeds. Measurement points were approximated by a 2nd degree polynomial, to allow thickness prediction in future processing:

$$t = 356.02 - 0.06714V_r + 5.04286\times10^{-6}V_r^2 \qquad (1)$$

where t is the layer thickness [nm], V_r – rotational speed of a spin-coater [rpm].

Table 2. Refractive indices of SiO_2 films
fabricated by various methods

Technology	Refractive index
HSQ SiO_2	1.398
Thermal SiO_2	1.450
PECVD SiO_2	1.477

Table 2 shows results of measurements of refractive indices for silica films fabricated by various methods. The refractive index for silica obtained from HSQ polymer has the lowest value of n equal to 1.398 whereas thermal dioxide has $n = 1.450$ at $\lambda = 632.8$ nm. The imaginary part of refractive index is very small: $k = 8.8\times10^{-6}$ at $\lambda = 632.8$ nm for HSQ SiO_2. In [2] it is stated that the real refractive index stays constant from 400 nm to 800 nm and is equal to 1.4. In the common PECVD process, the presence of impurities is possible as SiO_2 is obtained from silane gases e.g., SiH_4. SiO_2 from HSQ polymer was obtained by chemical polymerization, and some residues of solvent may remain in amorphous SiO_2 structures.

3.2. Reflectance

Reflectance was measured for silica films fabricated by various methods: thermal silica ($t = 200$ nm), PECVD ($t = 128$ nm) and for silica from HSQ ($t = 162$ nm) for various oxidation times: 0, 60 and 120 minutes (Fig. 3). Visible features of the spectra are most probably related to light interference within the films and onset of molecular absorption in near infrared region. Generally, spectra of PECVD, FOx and thermal oxides are very similar. However, the peak at $\lambda = 700$ nm does not occur for thermal silica. Other peaks are related to light interference in a film, for FOx layer ($t = 162$ nm, $n = 1.398$) the theoretical wavelengths of interference occur at $\lambda = 300$ nm and $\lambda = 181$ nm for the interference orders $m = 1$ and 2, in agreement with results shown in Fig. 3. The shifts of peaks for other samples are reflected in the differences of optical paths of light. As was mentioned previously, the maximum at $\lambda = 715$ nm (1.73eV) is related to molecular absorption. This peak is not observed in thermal oxide and is supposedly due to absorption of some sort of residues remaining after chemical processing or is a result of differences in the structure of oxides.

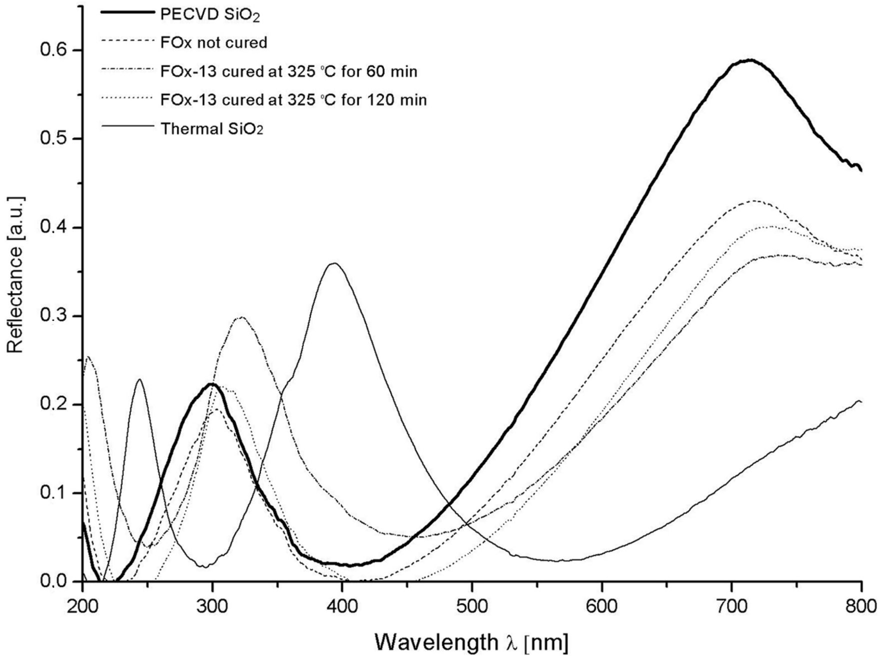

Fig. 3. Reflectance spectra of silicon dioxide prepared by various procedures

4. Conclusion

Optical properties of thin SiO_2 layers obtained from HSQ polymer were investigated. Comparison of FOx to PECVD and thermal silicon dioxide has also been reported. Beside standard application of FOx as a high resolution negative e-beam resist and other typical technological applications like mask in dry etching process, silica layers fabricated from HSQ polymer can be used in integrated optics. Possibility of achieving good quality films with a specific thickness and low refractive index is promising for usage of this material in fabricating grating couplers or optical surface for planar waveguides. The biggest advantage of HSQ polymer is the possibility to obtain amorphous SiO_2 thin layer on any surface, similar to PECVD silica, simply and relatively cheap.

Acknowledgements

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