Plasma processes for modifying optical properties of polymers

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A technology based on plasma etching has been developed to produce antireflective surface structures. By choosing thin initial layers and variable plasma conditions, a broad range of nanostructures can be obtained on various polymers. Specifically, a broadband antireflective effect can be achieved, which is less sensitive to incident angles of light compared to multilayer interference coatings. In addition, plasma etching of antireflective structures has been proven highly cost-effective during replication, especially for mass production, and may be a suitable alternative to common coating procedures.

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Antireflective structures have become rather well known since they were first discovered on the eye of a nocturnal moth by Bernhard in 1967[1]. The natural moth eye structure is characterized by periodically arranged bumps with dimensions well below the wavelength of visible light. Its structured surface acts as an effective antireflective medium featuring a decreasing refractive index from the substrate side to the surrounding air. The first technical implementation of antireflective structures was achieved using a holographic superposition of a light-exposed photoresist[2]. Such holographic processes have been enhanced and applied worldwide[3], but are mostly restricted to flat substrates. Various alternative procedures to generate stochastically arranged structures include the use of anodic oxidation of aluminum applied directly on a tool for embossing, flowerlike Al_2O_3 gel films, and reactive ion etching of a sol-gel film containing non-close-packed colloidal crystals[4−6].

Direct plasma etching of polymers to achieve antireflective structures on poly(methyl methacrylate) (PMMA) was first described in 2005[7]. This direct etching process introduced a production routine for antireflective structures on complex-formed substrates, such as Fresnel lenses. An advanced procedure developed in 2006 involved the use of additional deposition of a thin initial layer of prior etching[8]. From then on, a broad range of different morphologies exhibiting antireflective properties can be generated on almost all types of polymeric materials.

In this letter, we compared the properties of bump structures and sponge-like structures. Investigations using different plasma sources indicate the universal practicability of the etching technique.

Flat samples with optical-grade surfaces were prepared via injection molding of PMMA 7N, poly (methylmethacrylimide) (PMMI) 8817, Trogamid CX (Evonik Degussa AG, Germany), and Zeonex E48R (Zeon Nippon, Japan). Sheets of poly(etherterephthalate) (PET) Teteron OX50 (DuPont Teijin Films, U. K.) and triacetylcellulose (TAC) 80UVEP (Island Polymer Industries GmbH, Germany) were used as typical web mat erials. Further tests were carried out on the eyeglass material, polydiethyleneglycol-bis-allylcarbonate CR39.

The etching process was carried out in an APS904 vacuum deposition chamber (Leybold-Optics) equipped with an advanced plasma source (APS)[9]. Initial layers of TiO_2 and Ta_2O_5 were deposited by electron beam evaporation immediately prior etching using APS as ion source. A deposition rate of 0.02 nm/s was applied to obtain a precise thickness in the order of a few nanometers, which were controlled by the oscillating quartz method. The etching step was started immediately after depositing the initial layer. Oxygen, which was used as reactive gas, was partly ionized by the argon plasma emitted by a direct current (DC) plasma source during etching. Argon and oxygen ions were accelerated by a self-bias voltage to impinge on the substrate with an energy of up to approximately 120 eV. Alternative etching experiments were carried out using a Roth & Rau Microsys 400 chamber equipped with Tamiris ECR 220-f microwave plasma source (IonTech), Provac Taurion 800 evaporation chamber equipped with an radio frequency (RF) plasma source[10], and the RF etching station of an MRC-903 magnetron sputtering system.

After etching, SiO_2 layers with a thickness of 30 nm were deposited by ion-assisted deposition in the same vacuum process. Optical characterization of samples was carried out using Lambda 900 spectrophotometer (Perkin Elmer). The structured surfaces were visualized using a Phillips XL40 scanning electron microscope (SEM).

During the direct etching of PMMA and CR39 using an APS plasma source, a bump structure that was completely self-organized was formed within 4–5 min[7]. This process was restricted to a defined parameter window in terms of pressure, gas composition, ion energy, and time. A bump structure was also achieved on most other types of polymer substrates after increasing the etching time to 30 min at maximum. An aspect ratio suitable for antireflection was obtained after long-time etching on PET, TAC, and Trogamide, whereas most other materials did not show good antireflection properties at all. Some typical structures are shown in Fig. 1.

In particular, the low aspect ratio of the structure on Zeonex (Fig. 1(c)) shows that it is not able to significantly reduce reflection. Table 1 summarizes the reflection loss and the time required to achieve the highest

Table 1. Changes in Reflection, Transmission, and Etch Duration for Polymer Surfaces (Single Side) after Direct Plasma Etching without Initial Layers

Polymer	Average Transmission at 420–700 nm (%)			Residual Reflection at 550 nm (%)	Etch Duration (s)
	before Etching	after Etching	Difference		
Plexiglas 7N	92.4	95.8	+3.4	0.3	300
Pleximide 8817	89.4	91.0	+1.6	1.8	600
Trogamid CX	91.5	93.4	+1.9	1.0	600
Zeonex E48R	91.2	92.5	+1.3	2.6	1260
PET OX50	88.0	91.0	+3.0	0.4	555
TAC 80UVEP	92.0	94.7	+2.7	0.5	390
CR39	91.8	94.5	+2.7	0.6	300

Table 2. Changes in Reflection, Transmission, and Etch Duration for Polymer Surfaces (Single Side) after Deposition of Initial Layers Followed by Plasma Etching

Polymer	Average Transmission at 420–700 nm (%)			Residual Reflection at 550 nm (%)	Etch Duration (s)
	before Etching	after Etching	Difference		
Plexiglas 7N	92.4	95.5	+3.1	0.2	120
Pleximide 8817	89.4	92.7	+3.3	0.8	180
Trogamid CX	91.2	93.1	+2.9	0.9	300
Zeonex E48R	91.2	94.2	+3.0	0.3	250
PET OX50	88.0	92.3	+4.3	0.7	150
TAC 80UVEP	91.9	95.1	+3.2	0.2	120
CR39	91.8	95.1	+3.3	0.3	120

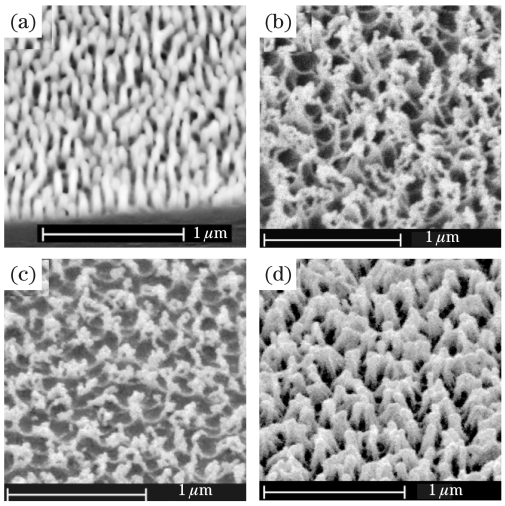

Fig. 1. SEM images of (a) Pleximide, (b)Trogamide, (c) Zeonex, and (d) TAC. Etching time is conducted based on Table 1.

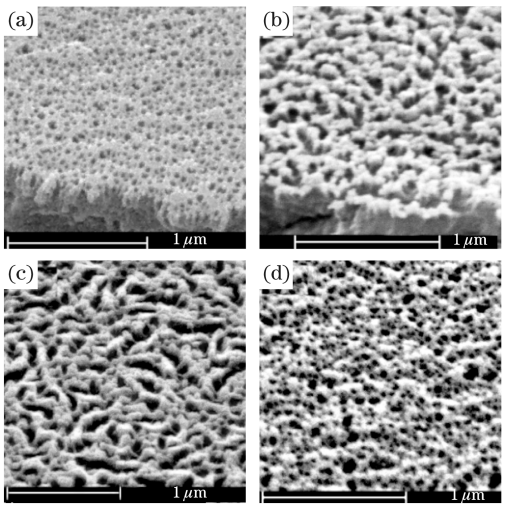

Fig. 2. SEM images of (a) Zeonex (Ta_2O_5 initial layer), (b) Zeonex (TiO_2 initial layer), (c) PMMA (TiO_2 initial layer), and (d) Trogamide (TiO_2 initial layer). Etching time was conducted based on Table 2.

possible transmission for all other materials included in this study.

An essential improvement in achieving antireflection properties on a variety of polymeric materials was obtained after the deposition of an initial layer prior the etching step[8]. Experiments show that a useful thin layer has to consist of a dielectric material. The layer is more likely nearly closed after deposition; by initiating inhomogeneous etching, a structure formation is achieved. Multiple structures can be produced on each polymer by varying the material and thickness of the initial layer, and the etch parameters. As an example, two qualitatively different structures on Zeonex are shown in Figs. 2(a) and (b), each of which were achieved using TiO_2 and Ta_2O_5 as initial layers, respectively, and with both structures exhibiting antireflective properties.

Typically, the structures achieve an initial layer that appear porous and with a surface resembling a sponge. For most polymer materials, this upgraded technique is more effective for obtaining antireflective properties compared to the direct etching method. In most cases, low reflectance level can be achieved at a considerably

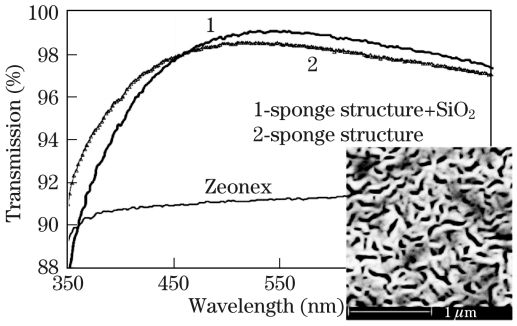

Fig. 3. Transmission spectra of etched Zeonex samples (both sides treated) with and without a protective top layer. The inset shows a SEM image (top view) of sponge-like structures on Zeonex protected by a 30-nm SiO_2 layer.

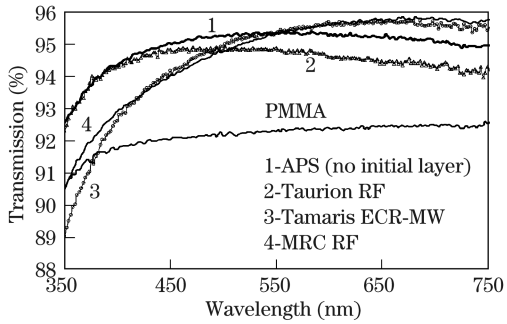

Fig. 4. Transmission spectra of PMMA before and after plasma treatment on one side (including 4% transmission loss caused by backside reflection) using different plasma sources. For etching experiments 2, 3, and 4, a thin TiO_2 initial layer was deposited prior etching.

shorter time. Similar results from this study are summarized in Table 2.

The basic disadvantage of most antireflective structures is their mechanical weakness. Surfaces with bumpy structures have to be handled very carefully; it is even practically impossible to clean them. For sponge-like structures, the stability of the surface can be considerably improved by depositing a silica layer on top of the structure. Optical properties do not degrade if layer thickness does not exceed about 30 nm. Figure 3 shows a structured Zeonex surface with a protective layer and the transmission spectra achieved with and without such a layer. The protected surface can be cleaned using a cloth and water or ethanol, for example, to remove a fingerprint.

After deposition of the initial layer, the plasma and ion treatment resulted in the ablation of the polymer material. Several plasma sources were tested for suitability. On PMMA, sponge-like structures could be produced after deposition of the initial layer using all plasma techniques tested. The transmission spectra of pre-coated PMMA samples etched on one side by different plasma sources are shown in Fig. 4. These spectra are the result of initial experiments without the optimization of the etch parameters.

In conclusion, an advanced technique that deposits an initial layer to produce antireflective structures prior etching has been developed. This method is effective in generating excellent antireflective properties on many polymer materials. The technique is not only limited to the use of a special plasma source; at least three different plasma sources were found applicable for the etching step. Sponge-like structures that resulted from this new technique can be mechanically stabilized, which makes them easier to clean compared to those with bump structures.

In the next phase of this study, the procedure will be adapted to generate antireflective structures via two methods: (1) by in-line sputtering techniques, and (2) by applying a roll coater on a web. In addition, investigations are in progress to obtain post-replication antireflective functions that is comparable to direct etching.

Embossing structures during manufacture by injection molding or hot embossing may be highly cost-effective, especially for mass production. In contrast, this etching technique provides a route for producing master structures based on planar and curved or micro-structured objects.

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