

PLASMA DEPOSITION OF OPTICAL FILMS AND COATINGS

Ludvik Martinu and Daniel Poitras

Groupe des Couches Minces (GCM) and Engineering Physics Department,
Ecole Polytechnique, Montreal, H3C 3A7, Quebec, Canada

Abstract

In the present work, we critically review the advances in the development of plasma processes for the fabrication of thin film high- and low refractive index optical materials, and for the control of plasma-surface interactions and film growth leading to desired multilayer or inhomogeneous optical layer systems.

1. Introduction

Development of the physics and technology of thin films has been largely stimulated by their use in optical systems for numerous "conventional" and "high-tech" applications. This includes in particular the dielectric coatings for optical filters (in a large sense the devices selecting a portion of the transmitted or reflected light, such as antireflective coatings, band pass filters, edge filters, hot/cold mirrors and others) and optical waveguides. As an example, close to 70% of glass production worldwide are provided with antireflective coatings, optical filters for thermal control, or with decorative coatings. This includes flat glass (window glass, picture glass, laminated glass, motor vehicle windshields and windows, skylight glass) and shaped glass (mostly lenses for precision instruments and for ophthalmic applications). The flat glass production worldwide is about 10^9 m²/year (almost half of it in the USA) which represents a U.S. market value of several billion US\$ [1,2].

Advanced applications include, for example, very narrow band filters for wavelength division multiplexing (WDM), interference color pigments for paints and antiforgery devices, low laser damage filters, and numerous others [3]. Optical thin film systems usually employ a step-index design (multilayers), and they are traditionally fabricated by physical vapor deposition, such as evaporation and sputtering, frequently assisted by ion bombardment (for example, refs. 1, 4 and 5).

With the development of new industrial and domestic products, frequently using polymer substrates, the optics industry searches for new approaches and technologies as well as for novel materials for optical films and coatings. The main forces which drive the research and development in this field are the following:

(i) Multifunctional character, or novel functions, and enhanced performance of optical coatings; beside their principal optical properties, the film selection criteria consider additional characteristics such as hardness, scratch-, abrasion-, and wear resistance, surface hydrophobicity or hydrophilicity, long-term chemical, thermal and environmental stability, electrical conductivity, optical non-linearity, and others. This calls for novel materials with substantially improved properties.

(ii) Adhesion of optical films and coatings to novel substrates, in particular polymers; these materials are known for their low surface energy and inertness, and new ways must be found to enhance film adhesion of films on polymers.

(iii) Deposition at high rates (>10 nm/s) should render the processes more cost-effective; further attributes include improved coating uniformity, ability to coat curved parts, and deposition at low substrate temperature.

2. PECVD of Optical Films and Coatings

Plasma enhanced chemical vapor deposition (PECVD), i.e. film growth using gas phase precursors activated in a glow discharge environment, can yield dielectric optical filters (the main subject of this presentation) based on high-low step index designs, similar to those fabricated by PVD. Technologically, acceptance of PECVD of thin films for optical applications has probably been delayed due to insufficient control of the complex plasma-chemical reactions, plasma-surface interactions, and process monitoring, and partially due to high equipment cost. However, recent advances in low pressure plasma processing, and in PECVD in particular, have greatly enhanced the interest in this technique for the fabrication of optical films, since it directly addresses all of the challenges mentioned above. Different aspects of the deposition process and the film characteristics have for many years been the subject of intensive research in our laboratory [e.g. 6-9], as well as by others [e.g. 10,11]. The most important attributes for using plasma are seen in the following:

a) Fabrication of *inhomogeneous optical films* in which the refractive index, $n(z)$, continuously varies as a function of depth z . The most significant optical filters of this kind use a rugate filter design (from latin: rugosus = wrinkled), where $n(z)$ varies sinusoidally. Absence of abrupt index changes (or abrupt interfaces) leads to the suppression of high-order harmonics, and appropriate apodization of $n(z)$ allows one to eliminate side lobes outside the band-pass wavelength; these characteristics are important, for example, for increased resistance to laser damage, cross-talk between neighboring channel frequencies in optical communication and others. In addition, absence of abrupt interfaces leads to a uniform distribution (or compensation) of internal stresses, and hence to better adhesion and mechanical integrity.

b) Control of plasma-chemical reactions and plasma-surface interactions allows one to optimize the film composition and microstructure: the films generally possess *high packing density* ($>95\%$); they are thus hard and environmentally stable. In one deposition chamber one can fabricate *multifunctional systems*; this includes, for example, scratch resistance, optical filter- and gas permeation barrier effects, followed by the top-layer hydrophobicity (or hydrophilicity). In addition, plasma pretreatment is becoming very attractive for surface modification of plastic substrates for enhanced adhesion [12].

c) PECVD provides *deposition rates* well above 1 nm/s, i.e. higher than other more conventional techniques. This applies particularly to high index materials. Different substrate shapes can be coated (flat, hemispherical, cylindrical, interior of tubes, etc.), while satisfying a frequently required thickness uniformity below 1.0% over more than 10 cm diameter on flat substrates.

d) A particular advantage of PECVD is its suitability to fabricate optical coatings on plastic substrates: besides their optical quality, the PECVD films exhibit enhanced adhesion, and they provide mechanical protection due to their hardness [13]. The generally superior

mechanical characteristics of PECVD coatings on plastics are attributed to the presence of a structured, physically thick *interfacial region* ("*interphase*"), formed by a crosslinked polymer layer (stabilization of the interphase) followed by a graded compositional profile frequently containing strong covalent bonds [9,14]. Formation of such an interphase is due to the synergistic effect of energetic species, originating from the plasma, with the exposed surface, namely free radicals, ions and VUV photons [12]. Using a multitechnique approach, the thickness of this interphase has been found to range from about 50 nm to 100 nm [9,14,15].

3. Conclusion

The present trends in PECVD of optical coatings include the following: (i) investigation of novel high-index materials ($n > 2.0$); (ii) industrial scale-up and process optimization (deposition rate, uniformity, reproducibility, *in situ* control); (iii) combination of multiple film functions; (iv) micro-mechanical performance; and other aspects.

References

- [1] Proc. 1st Int. Conf. on Coatings on Glass (ICCG), H.K. Pulker, K. Schmidt and M.A. Aegerter, eds., J. Non-Cryst. Solides, 218 (1997).
- [2] C.M. Lampert, Working Document for the International Energy Agency, Task 18, Advanced Glazing, June 1994.
- [3] S.M. Reiss, Optics and Photonics News, October 1997, p. 31.
- [4] J.A. Dobrowolski, Chapter 42 in the Handbook of Optics, 2nd ed., M. Bass, ed., Opt. Soc. of America, Washington DC, 1993.
- [5] F.R. Flory, ed., Thin Films for Optical Systems, Marcel Dekker, New York, 1995.
- [6] L. Martinu, J.E. Klemberg-Sapieha, and M.R. Wertheimer, Appl. Phys Lett., 54, 2645 (1989).
- [7] L. Martinu, J.E. Klemberg-Sapieha, O.M. Kuttel, A. Raveh, and M.R. Wertheimer, J. Vac. Sci. technol. A, 12, 1360 (1994).
- [8] D. Poitras, P. Leroux, J.E. Klemberg-Sapieha, S.C. Gujrathi, and L. Martinu, Opt. Eng., 35, 2693 (1996).
- [9] J.E. Klemberg-Sapieha, D. Poitras, L. Martinu, N.L.S. Yamasaki, and C. Lantman, J. Vac. Sci. Technol. A, 15, 985 (1997).
- [10] J.C. Rostaing, F. Coeret, B. Drevillon, R. Etemadi, C. Godet, J. Huc, J.Y. Parey, and V.A. Yakovlev, Thin Solid Films, 236, 581 (1993).
- [11] A.C. Greenham, B.A. Nichols, R.M. Wood, N. Nourshargh, and K.L. Lewis, Opt. Eng., 32, 1018 (1995).
- [12] E.M. Liston, L. Martinu, and M.R. Wertheimer, J. Adh. Sci. Technol., 7, 1091 (1993).
- [13] L. Martinu, in Plasma Processing of Polymers, R. d'Agostino, F. Fracassi, and P. Favia, eds., Kluwer Academic Publishers, The Netherlands, 1997, p. 247.
- [14] A. Bergeron, J.E. Klemberg-Sapieha, and L. Martinu, J. Vac. Sci. Technol. A, 16, 3227 (1998).
- [15] A.S. da Silva Sobrinho, N. Schuhler, J.E. Klemberg-Sapieha, M.R. Wertheimer, M. Andrews, and S.C. Gujrathi, J. Vac. Sci. Technol. A, 16, 2021 (1998)

