Soft plasma polymer coatings based on atomic polymerization

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ABSTRACT

Atomic polymerization (plasma polymerization) may be used to form soft polymer coatings of controlled physicochemical properties. Such coatings are utilized to construct functionally gradient and multilayered nanostructures of continuously or quasi-continuously varying physicochemical properties. Tailored nanostructures have high application potential for optical devices, photonic crystals, dielectric coatings, chemical sensors, separation membranes, biocompatible coatings, and polymer composites or nanocomposites of controlled interphase – composites without interfaces.

Keywords: thin films, soft coatings, plasma polymerization, nanocomposites

1   ATOMIC POLYMERIZATION

Plasma polymerization is a thin film-forming process based on atomic polymerization [1]. Monomer molecules are activated and fragmented during plasma process producing free radicals, electrons, and ions, and the highly reactive radicals recombine at substrate surface forming the thin film. The low-temperature plasma is a gentle but powerful tool for coating of substrates retaining their bulk properties. The substrate (glass, metal, ceramics, polymer, or composite) can be of planar, fibrous, or particulate form. The fragmentation of monomer molecule is controlled by the energy used for plasma process and the molecule can be fragmented in smaller species or even single atoms enabling the material construction at nanoscale synthesis [2]. The film thickness of deposited films can be from nanometers to microns.

2   SOFT PLASMA POLYMER COATINGS

Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background. This class of materials possesses a special characteristic, which distinguishes it from other plasma polymers – the ability to vary and control the degree of its organic/inorganic character (i.e., the carbon content) and the polymer cross-linking by the appropriate choice of fabrication variables [3,4]. This allows one to control many physicochemical properties over wide ranges resulting in an extraordinary potential for useful applications, which are only now beginning to be tapped. The organosilicon plasma polymers are widely recognized for their potential in optical, mechanical, and electronic applications. Mostly hard coatings are developed as protective layers, but we aimed at soft coatings using pulsed plasma. A reduction of plasma energy (power), but operated in several orders of magnitude, enabled us to control chemical composition and structure of soft plasma polymer coatings resulting in a wide range of mechanical, optical, and surface properties.

2.1   Chemical Properties

The elemental composition (Fig. 1) of soft plasma polymer coatings of hexamethyldisiloxane (pp-HMDSO), vinyltriethoxysilane (pp-VTES), and pure tetravinylsilane or TVS in a mixture with oxygen gas (pp-TVS/O$_2$) can be varied by deposition condition (RF power: 0.1 – 10 W, flow rate: 0.1 to 10 sccm, process pressure was 1 – 10 Pa).
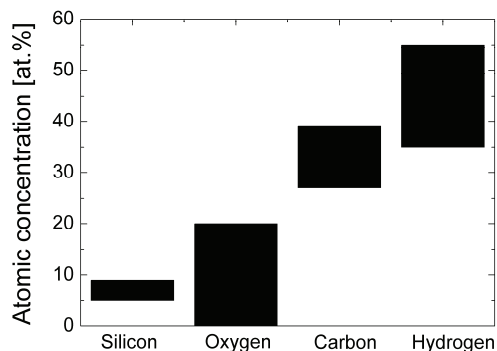

Figure 1: Elemental composition of soft plasma polymer coatings can be varied by deposition conditions.
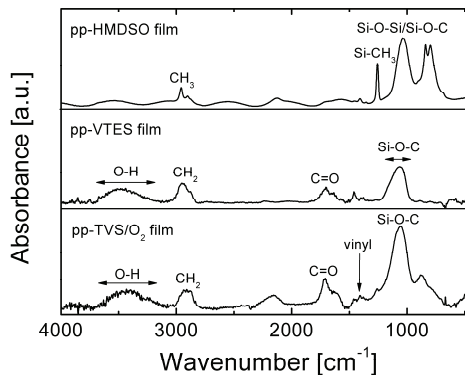

Figure 2: Infrared spectra characterize chemical structure of deposited films.

Chemical structure of coatings can be controlled by deposition conditions as well (Fig. 2). The functional group (e.g., ethoxy, vinyl) in monomer molecule can be preserved or eliminated and the new chemical groups ((e.g., hydroxyl, carbonyl) can be formed using suitable deposition conditions.

2.2 Mechanical Properties

The plasma polymer coating is deposited in a form of hydrogenated amorphous carbon-silicon (a-SiC:H) or carbon-silicon oxide (a-SiOC:H) alloy. Mechanical and optical properties of coatings are influenced by the bond energy and the level of polymer cross-linking. The Young's modulus of a-SiC:H alloy increases due to higher cross-linking at enhanced power (Fig. 3a). However, an incorporation of oxygen atoms into plasma polymer network reduces polymer cross-linking of a-SiOC:H alloy for RF power > 1 W. Similar behavior can be found for hardness (Fig. 3b).
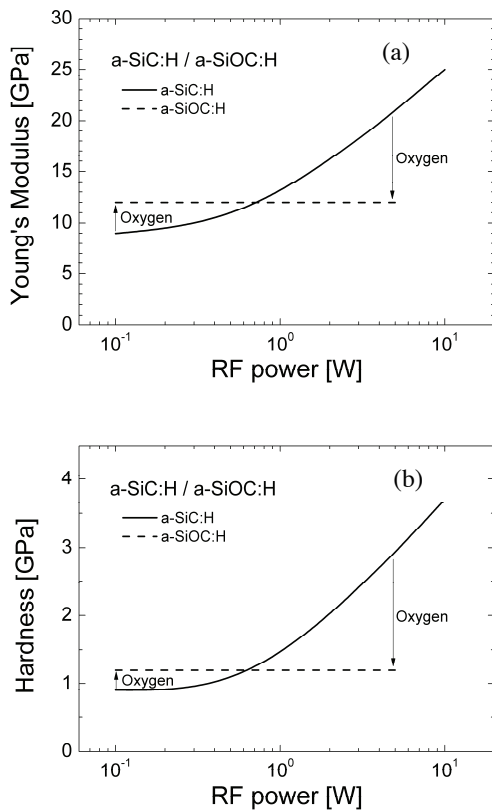

Figure 3: Mechanical properties controlled by RF power and amount of oxygen incorporated into plasma polymer network, (a) Young's modulus, (b) hardness.

2.3 Optical Properties

Dispersion curves for the refractive index and extinction coefficient are controlled by RF power and amount of

oxygen in plasma polymer network. The refractive index increases with enhanced power due to increasing optical density of polymer (Fig. 4a) but decreases due to stronger Si-O-C bonding species that are formed instead of weaker Si-C bonding groups (Fig. 4b).
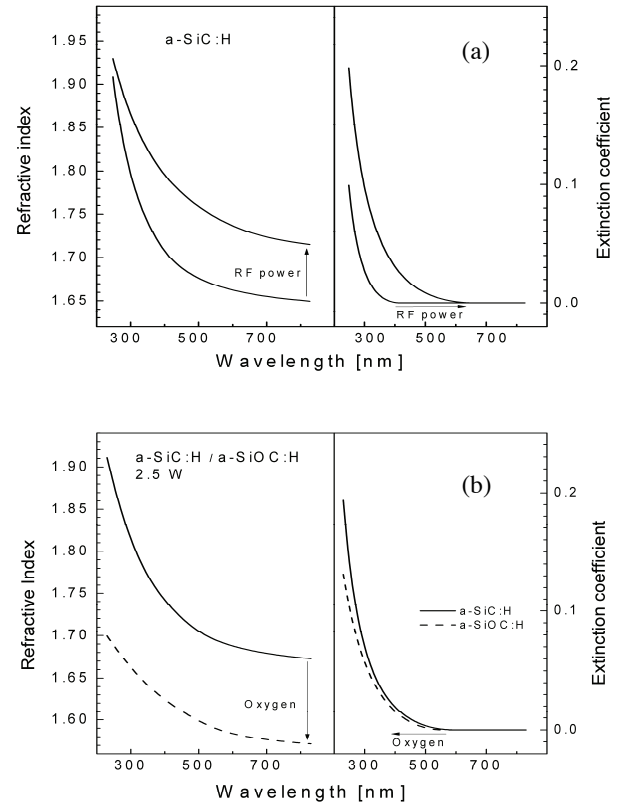

Figure 4: Dispersion dependences for refractive index and extinction coefficient (a) controlled by RF power and corresponding to a-SiC:H alloy, (b) controlled by amount of oxygen in polymer network of a-SiOC:H alloy.
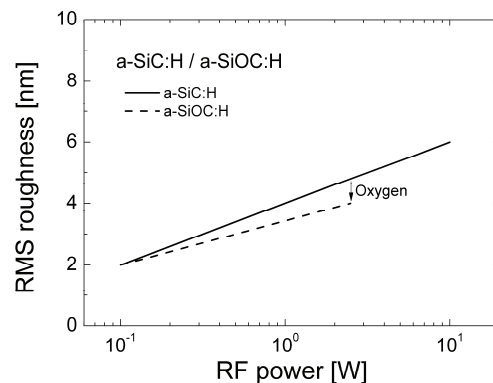
2.4 Surface Properties

Figure 5: RMS roughness of polymer coatings.

Surface morphology of soft plasma polymer coatings is influenced by RF power, amount of oxygen, and film thickness (Fig. 5).

Wettability of polymer coatings can be influenced by RF power and functional groups at coating surface. The total surface free energy (Fig. 6a) consists of dispersion and polar components. The dispersion component increases due to decreasing concentration of vinyl groups (pp-TVS) in polymer with enhanced power (Fig. 6b). The polar component increases due to increasing concentration of polar groups (OH, C=O) (Fig. 6c).
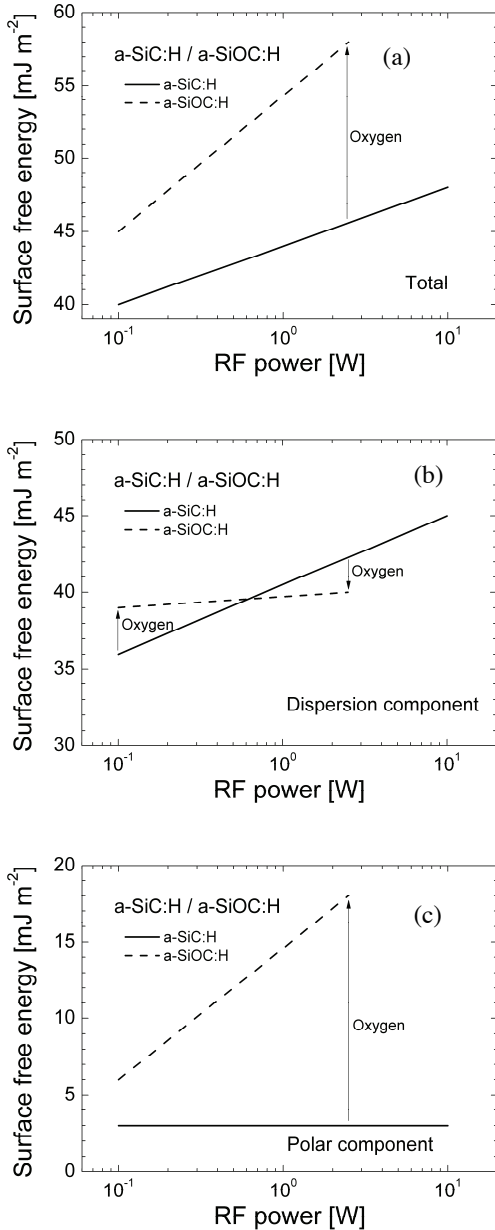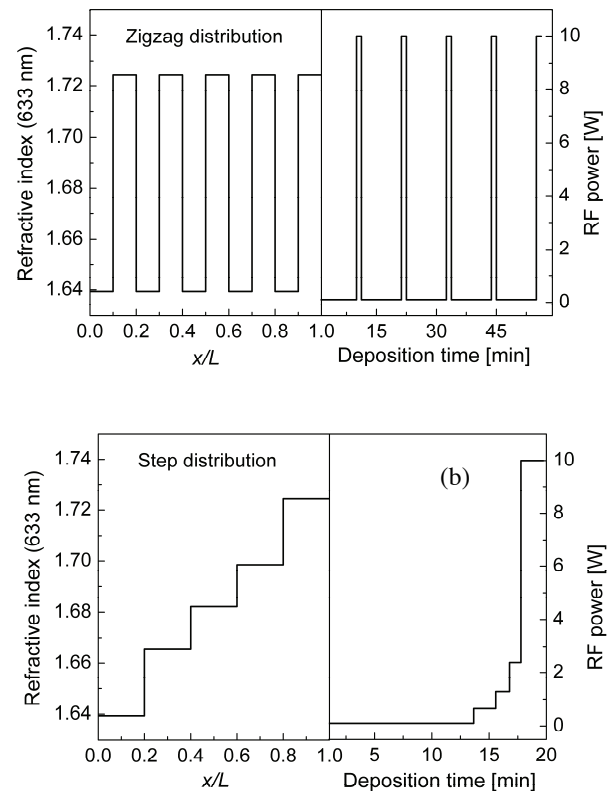

Figure 6: Surface free energy of polymer coatings, (a) total, (b) dispersion, and (c) polar component.

3 APPLICATION

Next progress was aimed at construction of functionally nanostructured films in a form of multilayers, with sharp of diffusive interfaces, and gradient coatings of physicochemical properties continuously varying from material A to material B. The deposited multilayered coatings were subjected to ellipsometric measurements that enabled us to distinguish individual layers in the layered structure and determine the layer thickness and its optical constants. Such tailored nanostructures may be used for optical filters, photonic crystals, and polymer composites or nanocomposites with controlled interphase.

3.1 Optical Devices

Soft plasma polymer coatings can be used to construct nanostructures from two polymers A and B using a layer-by-layer rotating system (Fig. 7a), or the coatings can be stack up varying properties of the individual layer stepwise (Fig. 7b), or the nanostructure of continuously varying properties can be constructed (linear gradient in Fig. 7c) to be tailored for specific application. Mechanical properties (Young's modulus, hardness) can be varied across the nanostructure in a similar way.
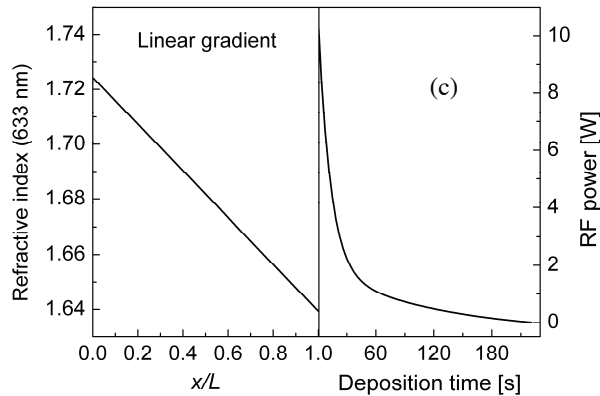
Figure 7: Refractive index across polymer coating and corresponding time-dependent RF power used to deposit the nanostructure, (a) zigzag distribution, (b) step distribution, and (c) linear gradient.

3.2   Polymer Composites

Soft plasma polymer coatings can be used to improve performance of polymer composites and enable to produce a new type of composites without interfaces. Soft plasma polymers were applied for nanocoating of glass fibers (GF) used as reinforcements for polyester composites and the functional nanocoating (pp-TVS/O2) overcame the industrial sizing (Fig.8).
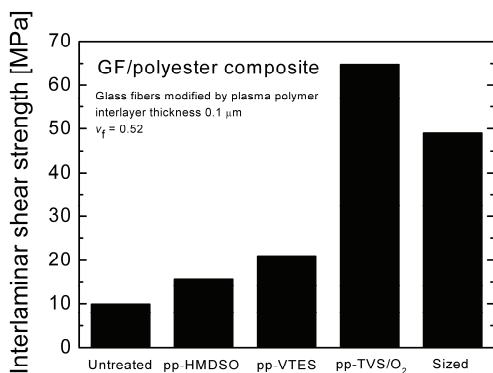

Figure 8: Interlaminar shear strength of GF/polyester composite reinforced by untreated, plasma coated, and industrially sized glass fibers.

3.3   Hybrid Coatings

Hybrid coatings may be deposited at higher powers to form soft grains in stiffer matrix (Fig. 9). The softer grains improve toughness of coatings and decrease the internal stress.
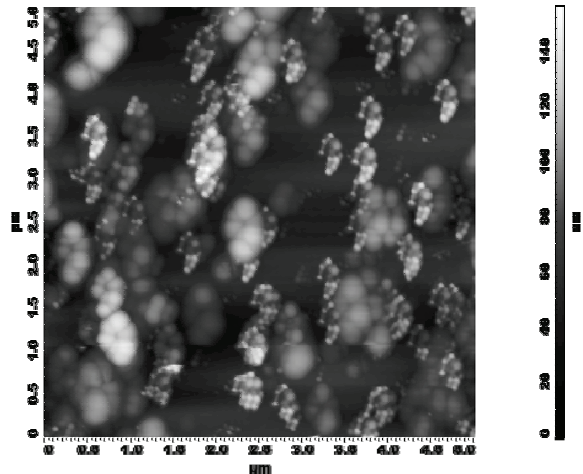

Figure 9: Hybrid coating including soft grains.

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