



Optical, mechanical and surface properties of amorphous carbonaceous thin films obtained by plasma enhanced chemical vapor deposition and plasma immersion ion implantation and deposition

Rafael G. Turri^{a,1}, Ricardo M. Santos^a, Elidiane C. Rangel^a, Nilson C. da Cruz^a, José R.R. Bortoleto^a, José H. Dias da Silva^b, César Augusto Antonio^a, Steven F. Durrant^{a,*}

^a Laboratório de Plasmas Tecnológicos, Universidade Estadual Paulista (UNESP), Av. Três de Marco 511, Alto de Boa Vista, 18087-180, Sorocaba, SP, Brazil

^b Laboratório de Filmes Semicondutores, Depto. de Física, Faculdade de Ciências, UNESP, Bauru, SP, Brazil

ARTICLE INFO

Article history:

Received 18 March 2013

Received in revised form 18 April 2013

Accepted 5 May 2013

Available online 13 May 2013

Keywords:

Ultraviolet–visible near infrared spectroscopy
Optical properties
Nano-indentation
Surface energy
AFM

ABSTRACT

Diverse amorphous hydrogenated carbon-based films (a-C:H, a-C:H:F, a-C:H:N, a-C:H:Cl and a-C:H:Si:O) were obtained by radiofrequency plasma enhanced chemical vapor deposition (PECVD) and plasma immersion ion implantation and deposition (PIIID). The same precursors were used in the production of each pair of each type of film, such as a-C:H, using both PECVD and PIIID. Optical properties, namely the refractive index, n , absorption coefficient, α , and optical gap, E_{Tauc} , of these films were obtained via transmission spectra in the ultraviolet–visible near-infrared range (wavelengths from 300 to 3300 nm). Film hardness, elastic modulus and stiffness were obtained as a function of depth using nano-indentation. Surface energy values were calculated from liquid drop contact angle data. Film roughness and morphology were assessed using atomic force microscopy (AFM). The PIIID films were usually thinner and possessed higher refractive indices than the PECVD films. Determined refractive indices are consistent with literature values for similar types of films. Values of E_{Tauc} were increased in the PIIID films compared to the PECVD films. An exception was the a-C:H:Si:O films, for which that obtained by PIIID was thicker and exhibited a decreased E_{Tauc} . The mechanical properties – hardness, elastic modulus and stiffness – of films produced by PECVD and PIIID generally present small differences. An interesting effect is the increase in the hardness of a-C:H:Cl films from 1.0 to 3.0 GPa when ion implantation is employed. Surface energy correlates well with surface roughness. The implanted films are usually smoother than those obtained by PECVD.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Plasma enhanced chemical vapor deposition (PECVD) may be used to produce a wide array of pinhole-free thin films with good adhesion to diverse substrates [1]. The deposited material may be tailored from soft polymeric to hard inorganic, depending on system parameters such as the monomers, comonomers, and their flow rates, the power applied to the discharge, etc. Plasma immersion ion implantation and deposition (PIIID) is accomplished by negatively biasing one of the electrodes so as to attract positive ions from the plasma. Ion irradiation influences the deposition processes and can alter the film composition and structure, thereby altering physical characteristics of the film such as, amongst others, its surface roughness, hardness, and optical transmission [2].

* Corresponding author. Tel.: +55 15 3238 3400x3437; fax: +55 15 3228 2842.
E-mail address: steve@sorocaba.unesp.br (S.F. Durrant).

¹ POSMAT student.

Amorphous fluorinated carbon, a-C:F, films are generally chemically inert and have low friction coefficients, thus making them suitable for tribological applications. The PECVD of a-C:H:F films has been extensively investigated by the Bari group [7–9] and others [10,11]. Plasmas containing ions and CF_x and CH_x species ($x=1-3$), and their roles in the formation of a-C:H:F films were intensively studied so as to better understand plasma–solid interactions, and led to the so-called Activated Growth Model [12]. More recently, PIIID of a-C:F films has been investigated [13,14]. Yao et al. [13] produced a-C:F films on silicon wafers from CH_4 – CF_4 mixtures with negative bias voltages, V_B , of up to 400 V. The F:C ratio in the films, as revealed by XPS analyses, decreased as a function of V_B . As confirmed by Raman spectroscopy, the films were polymeric at low V_B and became diamond-like at high V_B . Hardnesses increased from ~ 6 to ~ 14 GPa as V_B was increased from 60 to 400 V. No systematic changes in the water surface contact angle were observed as a function of V_B .

The degree of fluorination of a-C:F films was controlled in the 0–45 at% range using PIIID with CF_4 and a carbon cathode arc source [14]. Surface contact angles increased from $\sim 78^\circ$ to $\sim 105^\circ$ as the degree of fluorination was increased. The hardness, as measured using nanoindentation, decreased from 42 to 12.4 GPa, but even the most fluorinated film had a hardness far greater than that of PTFE (0.8 Pa).

The incorporation of nitrogen into a-C:H films obtained by PECVD of methane or acetylene with ammonia, methylamine or nitrogen usually reduces the carbon content, the deposition rate, the proportion of sp^3 -bonded elements, and the internal stress [15]. Films of a-C:H:N produced by PIIID exhibit better blood compatibility than low temperature isotropic pyrolytic carbon, and this improvement is due to the increase in hydrophobicity of the film caused by nitrogen incorporation and increased surface roughness [16].

Chlorine incorporation (~ 2.6 at%) in SiO_2 films produced by remote PECVD from $SiCl_4$, O_2 , Ar, H_2 mixtures stabilizes the material, leading to chlorinated oxides with properties close to those of stoichiometric SiO_2 [17]. Films with high chlorine content tend to be unstable on exposure to the atmosphere; the chlorine may be free or loosely bound. Similar studies have examined chlorine-doped SiO_2 [18] or plasma polymerized pyrrole or thiopene [19]. In the latter, the electrical conductivity of the doped polymer was about five orders of magnitude greater than that of the same polymer synthesized by plasma without doping [19].

Silicon-containing films such as a-C:H:Si:O and a-C:H:Si:N obtained by PECVD have been studied extensively over the last few decades [20–24]. Monomers such as hexamethyldisilazane [20], hexamethyldisiloxane [21–23a] and tetramethylsilane [24] are common. Applications include selective membranes for water and hydrophobic liquids [20], multilayer coatings [21], biomaterials [22] and humidity sensors [23a].

When ions at low energy (keV to MeV) interact with solids, elastic nuclear collisions and inelastic electronic collisions predominate [23b]. Elastic nuclear collisions dislocate atomic nuclei, increasing disorder and degrading the material. Inelastic collisions between ions and electrons produce excitations, chemical bond-breaking, and ionization.

In polymers or polymer-like materials ion irradiation can produce excited species, ionized species and free-radicals. The excited species can release energy via phonons or through bond-breaking. Depending on the film composition, side-groups can be fragmented, releasing species such as H, CH, F, CF, etc. As a result of such interactions unsaturated groups may be produced. Cross-linking may also be increased. Hydrogen loss and film compaction are well-known effects of ion irradiation of conventional polymers [23c]. Thus ion irradiation produces changes in both chemical structure and composition. Much used in electronic applications is

doping – the deliberate introduction of foreign atoms into the host material.

Some examples of the modification of the optical or mechanical properties of thin films via ion irradiation have been given above. A further example in optics is the increase in n from ~ 1.65 to ~ 1.78 induced by nitrogen implantation of plasma polymerized hexamethyldisilazane thin films [23d]. The irradiation produced OH and SiH groups, and increased unsaturation as witnessed by the appearance of C=O and C=N structures.

In the present study we examine some optical, mechanical and surface properties of a-C:H, a-C:H:F, a-C:H:N, a-C:H:Cl and a-C:H:Si:O films produced by both PECVD and PIIID, and whose chemical characterization is given elsewhere [3]. This characterization revealed that the a-C:H:F material contains <5 at% F; the a-C:H:N films ~ 1 at% N. The a-C:H:Cl films are highly chlorinated (~ 62 at%), while the a-C:H:Si:O films contain ~ 50 at% C, 20 at% O and 30 at% Si. The remaining films contain some oxygen at <6 at%. The elemental compositions were obtained by XPS, so the hydrogen content has been ignored. Only subtle differences are observed in the composition of the same type of film produced by the two deposition methods.

2. Experimental details

Two fabrication techniques, PECVD and PIIID, were employed to produce five pairs of films. The films were all based on amorphous hydrogenated carbon, a-C:H, but, in addition, fluorine, nitrogen, chlorine, and silicon and oxygen, were incorporated to produce a-C:H:F, a-C:H:N, a-C:H:Cl and a-C:H:Si:O films, respectively [3].

The deposition system consists of a cylindrical stainless-steel chamber fed gases from cylinders via regulators and needle valves or monomer vapors via a vial of liquid monomer sealed by a needle valve. The chamber contains horizontal parallel-plate electrodes. Radiofrequency power (45–100 W) is fed to the upper electrode via a matching circuit. For PECVD the lower electrode (anode) is grounded. For PIIID the upper electrode (cathode) continues to be fed RF power, while the lower electrode receives negative 20 μ s pulses of up to 4000 V produced using a RUP 6-20 supply (GBS Elektronik, GmbH, Germany). During deposition the system was evacuated continuously using a rotary vane pump. The partial pressures in the absence of the discharge were used as control parameters. For the deposition of each pair the chamber was fed the same monomer/comonomer under the same conditions of pressure and applied RF power. The five feeds (with the partial pressures in Pa), were, respectively, benzene (13.3)/argon (4.0), benzene (13.3)/sulfur hexafluoride (5.3), benzene(8.0)/nitrogen(5.3), acetylene(3.3)/chloroform(10.0), hexamethyldisiloxane (HMDSO)(13.3)/argon(6.7). The substrates were placed on the lower electrode for all the depositions. Deposition times of 15–25 min were used.

Film thicknesses were obtained from profiles of film step-heights recorded using a profile meter (Veeco, Dektak 150). The well-defined film edge was obtained by partially covering the glass substrate with an adhesive tape, which was removed following deposition.

Optical properties, namely the refractive index and absorption coefficient, were obtained from transmission ultraviolet–visible near infrared spectra taken at normal incidence in the wavelength interval from 300 to 3300 nm. A double-beam spectrophotometer (PerkinElmer Lambda 750) was employed with films deposited onto high quality quartz substrates.

Films for study by nano-indentation and atomic force microscopy (AFM) were deposited onto polished silicon substrates. Nano-indentation was undertaken using a Triboindenter–Hysitron system [25]. Hardness was determined as a function of depth,

Download English Version:

<https://daneshyari.com/en/article/5353025>

Download Persian Version:

<https://daneshyari.com/article/5353025>

[Daneshyari.com](https://daneshyari.com)