Structural and optical properties of brominated plasma polymers

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ABSTRACT

Novel brominated amorphous hydrogenated carbon (a-C:H:Br) films were produced by the *plasma polymerization* of acetylene–bromoform mixtures. The main parameter of interest was the degree of bromination, which depends on the partial pressure of bromoform in the plasma feed, expressed as a percentage of the total pressure, R_B. When bromoform is present in the feed, deposition rates of up to about 110 nm min^{-1} may be obtained. The structure and composition of the films were characterized by Transmission Infrared Reflection Absorption Spectroscopy (IRRAS) and X-ray Photo-electron Spectroscopy (XPS). The latter revealed that films with atomic ratios Br:C of up to 0.58 may be produced. Surface contact angles, measured using goniometry, could be increased from ~63° (for an unbrominated film) to ~90° for R_B of 60 to 80%. Film surface roughness, measured using a profilometer, does not depend strongly on R_B. Optical properties — the refractive index, n, absorption coefficient, $\alpha(E)$, where E is the photon energy, and the optical gap, E_g, were determined from film thicknesses and data obtained by Transmission Ultraviolet–Visible Near Infrared Spectroscopy (UVS). Control of n was possible via selection of R_B. The measured optical gap increases with increasing F_{BC}, the atomic ratio of Br to C in the film, and semi-empirical modeling accounts for this tendency. A typical hardness of the brominated films, determined via nano-indentation, was ~0.5 GPa.

1. Introduction

Surface bromination has been employed to improve the adhesion and wettability of polymers [1,2]. Diverse strategies have been used in such studies. Chanunpanich et al. brominated the surface of low-density polyethylene by brief exposure (~0.7 s) of this material to gaseous bromine followed by ultraviolet irradiation [3]. Analyses by X-ray Photoelectron Spectroscopy (XPS) suggested the presence of CBr, CHBr and CBr$_2$ groups on the surfaces of the treated material.

Bromination of poly(propylene) using plasmas fed bromoform was recently investigated [4]. The surface bromination was selective, producing covalent C–Br groups and little oxygen contamination. Such bromination of polymer surfaces finds application as steps in wet-chemistry grafting reactions. Ratios of Br to C atoms in treated polypropylene or polyethylene close to 1.0 may be obtained [5].

The deliberate production of brominated plasma polymers, however, has been less well studied. Feng et al. gave a succinct report of the production of bromine-doped a-C:H films by Radiofrequency Plasma Enhanced Chemical Vapor Deposition (RF PECVD) of bromoethene (ethyl bromide)–hydrogen mixtures [6]. Brominated plasma films have potential application as high-performance barrier membranes [7]. In addition, organic (CH$_x$) microshells doped with bromine have

been proposed as inertial-confinement fusion targets containing a deuterium–tritium mixture [8]. The starting materials were mixtures of hydrogen, trans-2-butene and bromoethane. A further application is the immobilization of single-strand DNA on nano-layers containing bromine produced by the pulsed plasma deposition of 2-bromoethylacrylate [9].

In the present study the RF PECVD of acetylene–bromoform (i.e. C_2H_2–$CHBr_3$) mixtures was examined. Films were characterized using profilometry, Infrared-Reflection Absorption Spectroscopy (IRRAS), XPS, contact-angle measurements, Ultraviolet–Visible Near-Infrared Spectroscopy and nano-indentation. Consequently, film chemical structure, composition and wettability, together with some optical and mechanical properties and their dependencies on the percentage of bromoform by pressure in the reactor feed, i.e. the partial pressure of bromoform to the total pressure, R_B, were evaluated. The dependencies of the measured characteristics on F_{BC}, the atomic ratio of Br to C in the films as determined using XPS, are also given.

2. Experimental

Films were produced by PECVD in a system described in more detail in the literature [10]. In short, it 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
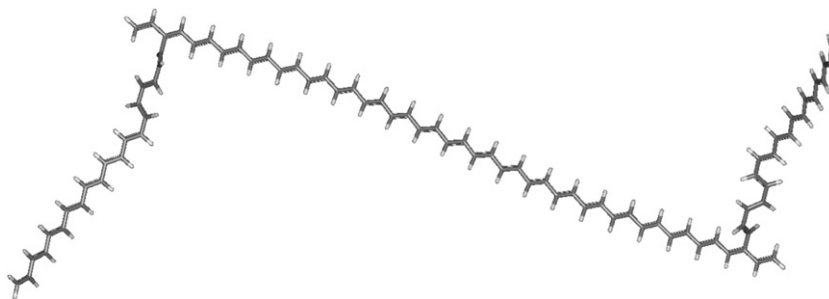
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Fig. 1. A typical 'molecule' used to simulate the film.

valve. The chamber contains horizontal, circular, parallel-plate electrodes. Radiofrequency power (13.56 MHz, up to 100 W) is fed to the upper electrode via a matching circuit. The lower electrode (anode) is grounded. Prior to deposition the system is evacuated to a base pressure of about 1.3×10^{-3} Pa. During deposition the system is evacuated continuously using a rotary vane pump (Edwards, 25 m^3 h^{-1}). The partial pressures in the absence of the discharge were used as control parameters. Films were deposited at an applied forward RF power of 60 W from acetylene–bromoform mixtures at a constant total pressure of 10.7 Pa. The parameter of interest was R_B, the partial pressure of

bromoform in the reactor feed expressed as a percentage of the total pressure. A deposition time of 15 min was used throughout.

Caution: Bromoform vapor is toxic, carcinogenic, and attacks any rubber seals or o-rings in the deposition system. Suitable safety measures should therefore be taken.

Substrates were placed on the lower electrode for all the depositions. Films for profilometric and goniometric (surface contact angle) analyses were deposited onto 1 mm thick glass substrates (Precision Glassline, USA). For both IRRAS and XPS analysis films were deposited onto polished 316 stainless-steel plates. Films for UVS analysis were deposited onto high quality, 0.5 mm thick, quartz substrates (Semiwafer, USA).

To measure film thickness, first a mask was used to partially cover the substrate, and hence deposition led to a well-defined step-height, from which the film thickness was obtained using a profilometer (Veeco, Dektak 3ST). Surface roughness, R_a, was determined from surface profiles.

Contact angle measurements were undertaken at 22 °C and a typical relative humidity of 50%, using a Ramé-Hart 100-00 goniometer in which a syringe dispenses a sessile drop (of volume around 0.2 μl) of distilled deionized water onto the film surface. The contact angle between a plane tangential to the drop surface and the film was measured from CCD images. Three drops placed at different surface sites on each film were measured. Ten measurements per site were taken.

Transmission infrared spectra were obtained in the 400 to 4000 cm^{-1} range at near normal incidence using a Jasco FT/IR-410 spectrophotometer (Jasco, Easton, MD, USA). X-ray Photoelectron Spectroscopy measurements were obtained using a VG Microtech ESCA 3000 (with MgK$_\alpha$ and AlK$_\alpha$ radiations) spectrometer. A take-off angle of 45° to the sample normal was employed in a hemispherical energy analyzer with an overall energy resolution of about 0.7 eV. Widescan and Gaussian deconvoluted C1s spectra were obtained. Shirley background correction was employed.

The optical properties – refractive index, absorption coefficient and optical gap – were calculated from knowledge of the film thickness, the refractive index of the substrate, and transmission ultraviolet–visible spectra taken at normal incidence in the wavelength interval from 300 to 3300 nm. A double-beam spectrophotometer (Perkin Elmer Lambda 750) was employed to acquire the spectra.

Computational methods were also used to calculate the theoretical optical gap of a 'molecule' of the film as deduced from the IRRAS and XPS data. A standard molecule ($C_{86}H_{88}$), as shown in Fig. 1, was employed. The semi-empirical method PM3 [11], available in the MOPAC [12] package, was used to calculate the equilibrium geometry of the modeled molecules. The results obtained were used as input in the ORCA package [13], using the semi-empirical method ZINDO/S to simulate the absorption spectrum of the material. Using the approach developed by Zerner and Ridley [14], the optical gap was obtained from the simulated absorption spectrum. To avoid problems related to different gap values obtained for molecules where the bromine
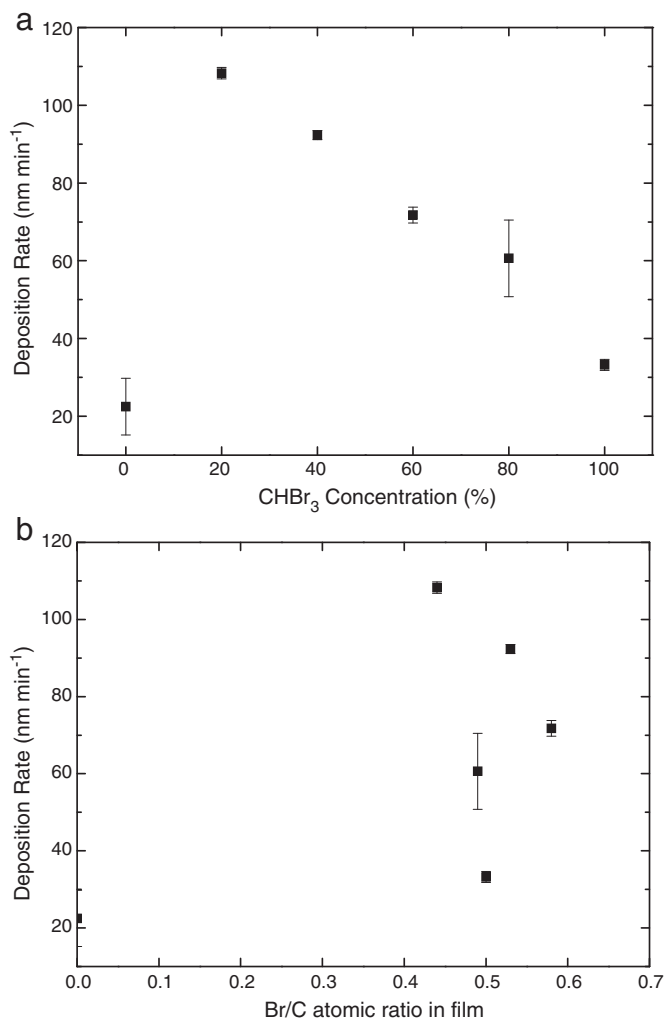

Fig. 2. a. Deposition rate as a function of R_B. b. Deposition rate as a function of F_{BC}.