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Structural properties of ultraviolet cured polysilazane gas barrier layers on polymer substrates

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ABSTRACT

Perhydropolysilazane (PHPS) conversion to silica through high energy ultraviolet irradiation has been studied. Precursor conversion speed and structural properties of the UV cured PHPS have been investigated and showed that this conversion method is fast but that complete conversion into silica is not achieved in an oxygen depleted atmosphere for layer thicknesses higher than 30 nm, resulting in a composite structure with concentration gradients. We further show that Fourier transform infrared spectroscopy data allow investigating the local structure and composition over the depth of the obtained layers. Gas permeability of the thin UV cured PHPS layers deposited on polymers has been studied. We used a high sensitivity permeation measurement technique to determine water vapor and oxygen permeabilities of the barrier layers and show the correlation between helium, oxygen and water permeability of these materials. Oxygen and water vapor transmission rates of respectively 0.06 $cm^3/m^2/day/bar$ and 0.2 $g/m^2/day$ have been obtained with layers deposited on a polymer substrate.

1. Introduction

Numerous devices or products need to be protected from oxygen and moisture while remaining transparent and flexible. In the case of organic electronics encapsulation, the barrier materials should be obtained at very low costs to remain in accordance with the devices' low prices.

A way to obtain such gas barrier materials is adding a thin dense inorganic layer on a polymer substrate. Usually, thin silica and silicon nitride layers are used for this purpose, as they are easily deposited by plasma enhanced chemical vapor deposition, and lead to oxygen transmission rates (OTR) and water vapor transmission rates (WVTR) of about 0.01 $g/m^2/day$ and $cm^3/m^2/day/bar$ respectively [1–3]. The main limitation to the efficiency of these barrier layers is the defects in the coating that may occur either during the deposition process (pinholes) or shortly after (cracks). Although permeability should theoretically decrease with material thickness, thick layers on polymer substrates are more subject to cracking and delamination than very thin ones [4].

As vacuum deposition techniques are considered to be expensive and to present a low throughput, especially when several layers are deposited, there is a growing interest in solution deposited precursors, which are in turn cured into a thin homogeneous inorganic layer. Numerous organosilicon precursors such as silanes and silazanes are of potential interest [5]. Among silazanes, perhydropolysilazane (PHPS) is a very versatile precursor. It is an inorganic polymer composed only of Si–N, Si–H and N–H bonds. PHPS conversion into dense silicon oxide or nitride is achieved through high temperature curing [6–9] or with lower temperature curing assisted by a catalyst or a high level of moisture [10–12]. Since curing temperature of coatings on polymer substrates is limited, the latter is preferred, but these alternative curing routes provide limited oxygen and water barrier improvement factors and lead to materials with insufficient gas-barrier properties [13].

Naganuma [14] and Prager [15] have studied PHPS conversion through UV irradiation and obtained promising permeabilities for barrier layers on polymers even though the exact conversion process leading to PHPS oxidation is not fully understood. This UV curing process is a breakthrough as it allows for the conversion of silazanes in much milder conditions than usual pyrolysis or hydrolysis, opening a large range of applications such as high throughput coating on polymer substrates. Prager et al. have employed vacuum ultraviolet (VUV) irradiation from different sources at wavelength between 172 and 222 nm, which requires operating at low oxygen partial pressure in the reaction chamber as oxygen absorbs such high energy photons to form ozone. Nevertheless it has been shown with time of flight-secondary ion mass spectrometry (TOF SIMS) analyses of the cured samples that the oxidation takes place at the top surface of the layer and progresses inwards. They reported an oxygen barrier improvement factor of two orders of magnitude with a single 150 nm deposit of PHPS on a polyethylene terephthalate

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(PET) substrate. The aim of our work is to shed some light on the oxidation process and the chemical structure of the layers cured through this UV irradiation and to investigate the gas barrier properties provided by thin layers of these materials deposited on a transparent thin and flexible polymer substrate. The understanding of the conversion mechanism and resulting layer chemical structure led to optimization of the inorganic layers for their implementation in multilayer gas barrier materials [16].

2. Experimental details

2.1. Barrier film preparation

For curing rate studies, perhydropolysilazane in di(*n*-butyl)ether (NN-120-20 (A), Clariant) with concentrations from 1 to 20 wt.% was spin coated (1000 rpm) on 50 × 50 mm^2 silicon wafers (725 μm) resulting in dry layers of PHPS of 30 to 600 nm. Ultraviolet curing was performed in a gastight aluminum casing equipped with two Heraeus Noblelight NIQ 65XL low pressure mercury lamps (Hg LP). These lamps emit in the UV domain at 254 nm (20 W) and in the VUV domain at 185 nm (5 W) and their distance to the sample holder was 20 mm. A continuous gas sweeping is applied with a row of vents placed along the lamps, allowing them to cool and flushing the atmosphere in the chamber. The gas sweeping consists of a tunable mixture of 99.9% pure dry nitrogen and 5% O_2 in dry nitrogen. An electrochemical probe oximeter is placed near the surface of the sample. Before beginning the curing of the sample, atmosphere is purged with nitrogen during 10 min (8 L/min) and lamps are allowed to heat during 5 min to reach their nominal power. The curing takes place with a partial pressure of oxygen at the surface of the sample inferior or equal to 1%.

To monitor the conversion rate, an infrared spectrum was immediately recorded after deposition and the curing was monitored by periodically recording infrared (IR) spectra. Fourier transform infrared (FTIR) spectra were recorded in transmission mode on a ThermoElectron Corporation Nicolet 5700 spectrometer, taking the bare silicon wafer as blank. A reference for perfectly converted material into silica was made by pyrolyzing a coated sample in a furnace at 600 °C under air during 30 min.

Thickness and refractive indexes were measured after the curing by spectroscopic ellipsometry with a Horiba Jobin Yvon Uvisel spectrometer on the spectral region of near UV and visible light from 1.5 eV to 6.0 eV and an incidence angle of 70°.

TOF SIMS measurements have been realized with a Iontof V spectrometer equipped with 25 keV, 1.5 pA Bi^+ and 2 keV, 128 nA Cs^+ ion sources.

For the test of the actual encapsulation efficiency, barrier foils were prepared by coating a 50 μm PET Melinex 501 substrate with the perhydropolysilazane solution by means of a bar coater (Erichsen K Hand coater set).

2.2. Barrier properties measurements

Permeation measurements were performed with a patented homemade permeameter (Fig. 1) [17]. In our device, the sample to be tested separates an upstream chamber filled with the gas of interest and an ultra-high vacuum chamber enclosing a quadrupolar analyzer and ion trap detector MKS E-Vision+ mass spectrometer. The measurement cell is connected to a gas bench equipped with different permeating gas reserves and a primary vacuum unit, allowing control of the upstream side atmosphere.

The mass spectrometer detects an ion current proportional to the permeating rate of the upstream gas. Ion current is then normalized by the actual measurement of pressure on the upstream side. Relation between ion current and absolute permeating rates is known by testing permeabilities of known reference polymers such as PET. Using such a device allows one to use isotopes as permeant, thus increasing the sensitivity of the measurement by discriminating the signal from the ambient atmosphere contamination. Thus, water permeation measurements were performed with heavy water 99% D_2O (Eurisotop) at a pressure of about 40 hPa, oxygen permeation measurements were performed with 99% $^{18}O_2$ isotope (Eurisotop) with an upstream pressure of about 200 hPa. Helium permeation measurements have been done with the same pressure of abundant stable ^4He isotope, as normal atmosphere is helium depleted. Helium is a very small molecule; it therefore diffuses so fast in barrier layers that a steady state is reached nearly instantly. Thus, helium permeation method is advantageous as it allows the screening of a large number of samples in a short time span.

3. Results and discussion

3.1. High temperature curing of PHPS

The pyrolysis of a PHPS layer during 30 min at 600 °C is sufficient for achieving its total conversion into silica [13]. This allows comparing both as deposited material and a perfectly converted material. As described in Fig. 2, transmission FTIR spectrum of as deposited (solid line) PHPS shows notable and attributable vibration bands which are

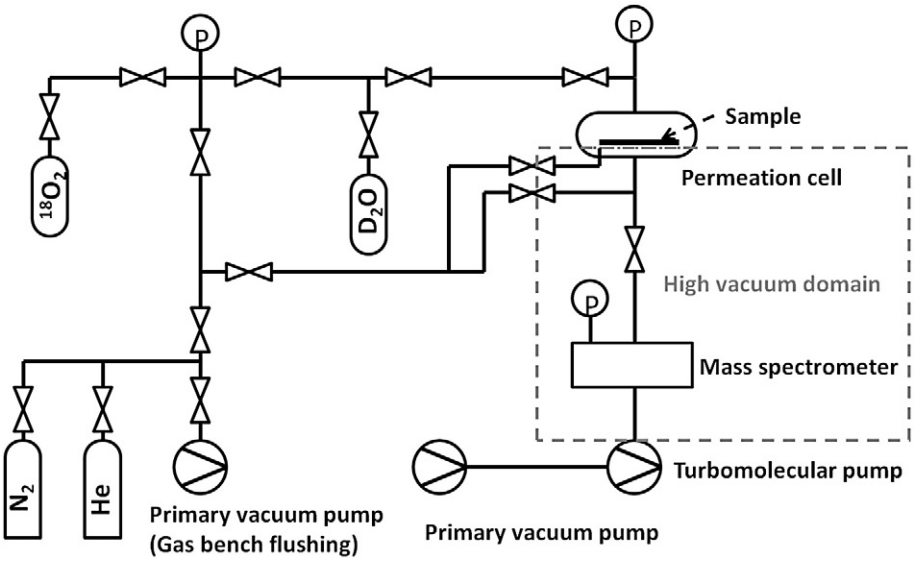

Fig. 1. Scheme of permeameter developed at CEA-INES [17].