DUAL-FREQUENCY PLASMA SURFACE MODIFICATION OF POLYIMIDE THIN FILMS

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Abstract

In this work, a complex investigation of the film surface composition, chemical bonding, optical properties and moisture uptake of dual-frequency plasma modified polymer films was carried out. Plasma treatment was performed in a PECVD deposition chamber using two r.f. power supplies operated in a switched mode for NH_3 and N_2O low pressure gas discharge generation. The application of low pressure plasma modified polymer films in moisture sensors and waveguide structures is proposed.

3. Introduction

Polymer thin films such as polyimide (PI) find extensive use in aerospace and electronic application. The physical properties of these films may be tailored for special sensor applications by plasma surface modification which alters the nature of the surface without changing the properties in the bulk. However, the effectiveness of a plasma-assisted surface treatment depends on a number of process parameters such as process gas composition, total gas flow rate, operation pressure and frequency of the electrical excitation source. Radio frequency (r.f.) plasma surface modification has been used successfully since the 70's for improving the adhesive characteristics and the hydrophility of PI [1]. DuPont's Kapton® polyimide (PMDA-ODA) has been plasma-treated in He, O_2 and NH_3 r.f. (13.56 MHz) discharges for improving aluminum adhesion [2]. Helium plasma treatment was the most effective in this case while NH_3 plasma processing induced a drastic degradation of the PI surface. Low frequency (Hz to kHz) power modulated r.f. low pressure NH_3 discharges were applied for preferential grafting of $-NH_2$ groups on polyethylene substrates [3]. Low frequency (50 Hz) plasma modification of PI and polypropylene was performed in [4]. The increase of PI hydrophility after plasma treatment was attributed to the appearance of surface charge states and in less degree to the formation of polar groups on the surface. A dual frequency approach has been used for surface modification of polyethylene and polyimide [5]. Microwave and r.f. powers were applied simultaneously to a low pressure discharge to benefit from the high concentration of active species in microwave discharges and the controlled ion bombardment of r.f. biased surfaces. A switched plasma technique is known for PECVD deposition of silicon nitride [6] and silicon carbide [7,8] films. In this case, film stress is controlled by altering the ratio of low-frequency (100 to 400 kHz) and high frequency (13.56 MHz) power cycles.

In this work, a complex investigation of film surface composition, chemical bonding, optical properties and moisture uptake of polymer films modified in 100k Hz/13.56 MHz dual-frequency NH_3 and N_2O low pressure plasmas was carried out.

4. Experimental

The polyimide investigated in this study was DuPont's polyimide PI2566 [6FDA-ODA; hexafluoroisopropylidene bis(phtalic anhydride-oxydianaline); $(C_{31}H_{14}N_2O_5F_6)_n$] (cf. Fig. 1). It was selected for investigation due to its comparable low optical anisotropy and the therefore possible application in wave-guide structures [9]. Polyimide films were prepared by spin-coating of commercially available polyamic acid /N-methyl-2-pyrrolidone solutions onto 3" silicon wafers which served as convenient substrates. After deposition of the polymers the solvent was removed at 90 °C for 30 min, and films were remaining with a thickness between 1.0 and 3.5 μm on the substrates. After prebaking the precursor system was baked to convert into polyimide structure at 400°C for 60 min. The completion of this chemical reaction was checked by FTIR spectroscopy.
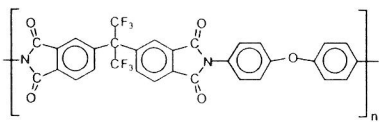

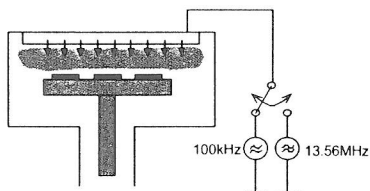Figure 1: Chemical structure of PI2566

Figure 2: Plasma treatment set-up

The polymer films were modified at room temperature by low pressure plasma treatment in NH_3 and N_2O discharges using a Plasmalab 80^+ PECVD chamber (Oxford Plasma Technology). Two r.f. power supplies were used in a switched mode, a high frequency (HF) unit (13.56 MHz) for a soft surface modification and a low frequency (LF) unit (100 kHz) to enhance ion bombardment on the as-modified film surface (Fig. 2). The typical plasma treatment was performed 1 minute at a substrate temperature of 25°C, a pressure of 0.27 mbar, gas flow rates of 20 sccm and 100 sccm for NH_3 and N_2O, respectively, low frequency and high frequency powers of 20W each, HF and LF cycle times of 10 s each. Variations of the treatment parameters are depicted on the corresponding figures. Ammonia discharges generate mainly neutral fragments of NH_3 molecules including NH_n (n=1,2), H and H_2 [3].

The chemical structure of the modified polymer layers was investigated by Attenuated Total Reflection (ATR)-FTIR spectroscopy. ATR measurements were carried out on a Bruker spectrometer IFS 66 with a „Golden Gate" unit (Ge crystal) for 200 scans with a resolution of 4 cm^{-1}. In this case, the penetration depth is 166-1106 nm at 4000-600 cm^{-1}. The chemical changes only in the surface regions were studied by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5702 electron spectrometer. The sampling depth of this technique amounts about 8 nm. The atomic ratios of the elements were estimated using tabulated sensitivity factors. The spectra were referenced to the C 1s line at 284.8 eV arising from C-C or C-H bonds. The core level peaks have been analyzed by means of a best Gauss-Lorentz fit computer program with background subtraction. Curve-fitting quality was evaluated by chi-convergence.

Refractive and absorption index spectra and films anisotropy were calculated from main ellipsometric angles Δ and Ψ measured with J. A. Woollam spectroscopic ellipsometer. Using

of 10 different angles of incidence allowed us to perform the refractive index depth profile calculations. The experimental data was analyzed with the software package WVASE32, which is based on least-square regression analysis to minimize the differences between measured and calculated values. The moisture uptake $c_s(\varphi)$ was determined as a value of the relative mass uptake in the polymer film of polymer coated silicon wafers. An enclosed precision balance was used with an accuracy of about 20 μg under variable, tightly controlled ambient conditions (temperature and relative humidity uncertainties were $\Delta T = \pm 0.5$ K and $\Delta\varphi = \pm 2$ % rh, respectively).

6. Results and Discussion

The changes in polymer surface composition after plasma exposure determined by XPS are shown on figure 3. Due to their higher binding energy, fluorine containing bonds are most stable under plasma treatment. Oxygen attack increases the surface fluorine concentration because the surface is partly destroyed by ion bombardment and some of their constituents are volatized while hydrogen and NH attack give a slight decrease. A nitrogen enriched surface was obtained after all plasma exposures. The N 1s spectrum shows only the imidic nitrogen at 400.4 eV which was shifted with increasing nitrogen surface concentration to lower energies probably due to linear >C=N (399.3 eV [10]) groups formation. This agrees with the nitrogen predominant amine (N-H) group bonding at the polyimide surface after NH₃ dual-frequency plasma treatment [5]. The enrichment was small after N₂O treatment and pronounced after NH₃ exposure. The vice versa was obtained for the oxygen surface concentration. After ammonia treatment traces of residual gases were found in the polymer composition. Aluminum traces sputtered from the reactor electrode and wall areas were obtained on the polymer surface after high power operation (200W HF). Traces of silicon observed in the untreated sample were probably unintentionally incorporated during polymer synthesis. The C 1s spectrum consists of 4 peaks respectively assigned to bonds of the oxydianiline part [5] or C-C, C-H bonds [10] at 284.7 eV, C-O-C, >C=N and aromatic carbon bonds to more than one carbonyl at 286 eV, N-C=O [10], C=O [5] and CF₃-C-CF₃ [11] at 288.2 eV, CF₃ at 292.7 eV [11].
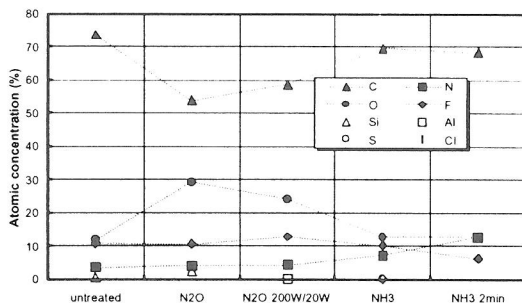

Figure 3: Surface concentration of atomic elements in dependence on plasma treatment. Note, that hydrogen can not be determined by XPS.

Changes of the C 1s peak areas after plasma treatment are depicted on figure 4a. Benzene rings are destroyed by plasma exposure and oxidized in the N₂O plasma or nitrided in the NH₃

one. This is confirmed by a slight shift of the 284.7 and 286 eV peaks to higher energy with N_2O plasma treatment and a vice versa shift after NH_3 plasma treatment. The O 1s band was resolved into three components at 530.8, 531.6 and 532.6 eV (Fig. 4b). They were assigned to O-H (531.4 eV [12]), imide carbonyls C=O (532 eV [10]) and C-O-C linkages (533.3 eV [10]). A rearrangement of surface bonds toward C-O-C ones to form a more stable surface was obtained after long-term air storage. At the same time, the total oxygen surface concentration remained nearly constant. Ammonia plasma treatment increases the surface concentration of O-H groups. The obtained surface restructuring upon plasma exposure is similar to that of PI2566 surface modification by ion beam implantation [13]. In the latter case, the imide and aromatic groups are partly destroyed and aromatic structure is degraded by hydrogen abstraction up to partial graphitization. Contrary to ion beam modification, the O+N/C ratio at the surface increases after plasma treatment
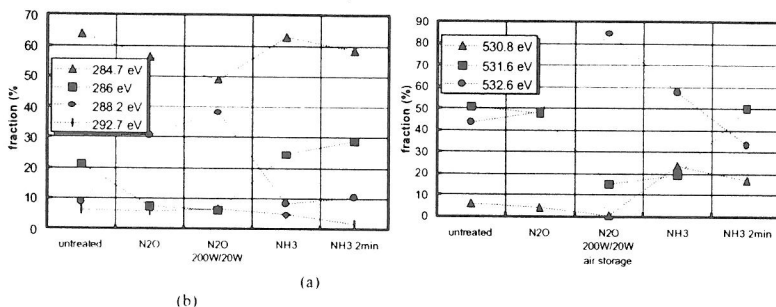

Figure 4: Changes of XPS peak fraction in dependence on plasma treatment, a – C 1s, b – O 1s

ATR measurements resulted in practically no changes of the IR-spectra (Fig. 5). Therefore, the polymer modification by plasma treatment is in our case limited to a narrow surface region.
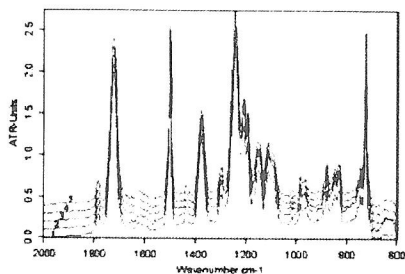

Figure 5: Infrared absorbencies of untreated (1), NH_3 plasma treated (2,3) and N_2O plasma treated (4,5) polymer thin films, 3,5 - 200W/20W LF/HF power ratio
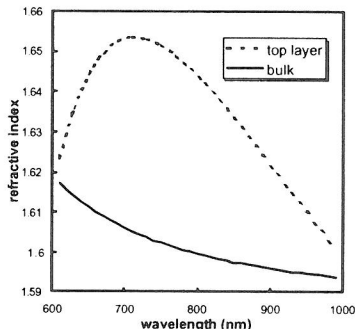
Figure 6: Spectral dependence of the refractive index

Ellipsometry reveals a slow etching process (rate about 2 nm/min) in the NH_3 discharge during low LF power treatment and the formation of a 35 nm thick top layer which has a different spectral dependence of the refractive index (Fig. 6) after high LF power (200W)

surface modification. The top layer thickness includes obviously also a contribution due to surface roughness. Applying a one-oscillator fit of the refractive index, a decrease of the oscillator energy from 7.3 eV (corresponding to the $^1A_{g1}$-$^1E_{u1}$ transition of benzene) to 1.75 eV results. This gives evidence of π electrons bonded in more graphitic rings or delocalized over several rings [14].

Moisture uptake depends on the mass of the polymer itself, so it is useful to relate the mass of the absorbed water to the mass of the dry polymer. Thus, a saturation concentration c_s can be defined as:

$$c_s(\varphi,T) = \frac{m_{water}(\varphi,T)}{m_{dry\,polymer}} = \frac{m_{coatedWafer}(\varphi,T) - m_{coatedWafer}(\varphi = 0\%\,rh)}{m_{coated\,Wafer}(\varphi = 0\%\,rh) - m_{uncoatedWafer}}. \tag{1}$$

At 100% relative humidity, the saturation concentration reaches its maximum $c_{s,max}$. Figure 7 compares adsorption isotherms of the N_2O plasma treated and low dose (10^{13} cm^{-2}) boron ion implanted PI2566 thin films [13]. All curves are slightly nonlinear and can be described by the Freundlich's formula [15]:

$$c_s(\varphi) = c_{s,max} \cdot \varphi^n \tag{2}$$

where $c_{s,max}$ is the maximum saturation concentration, ö the relative humidity in the range between 0 and 1, and n the Freundlich's coefficient. A one minute plasma treatment gives n≈1. Thus, plasma treatment could be used for moisture uptake linearization of humidity sensors where film swelling is monitored by a corresponding change in piezoresistance caused by plate bending of a polymer-silicon double-layer sensor. The maximum saturation concentrations are depicted in figure 8. The chemical surface modification saturates within a treatment time of one minute.
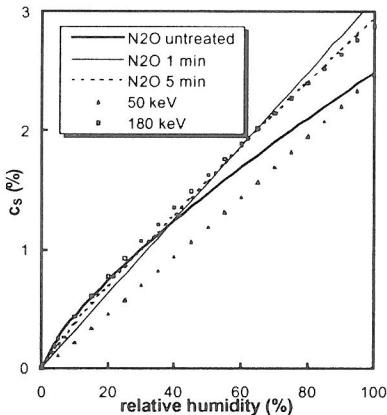

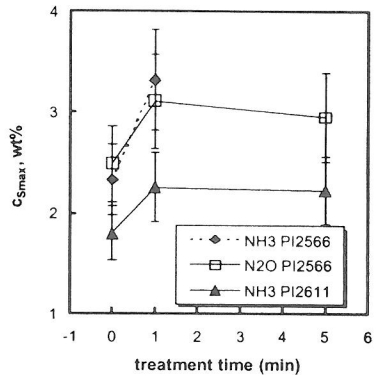Figure 7: Adsorption isotherms of plasma surface modified and ion implanted PI 2566 films

Figure 8: Dependence of the maximum saturation concentration on plasma treatment time

The observed increase in moisture uptake is correlated with the well known increase in surface wettability of plasma treated polymer films. This increase is related to the formation

of polar groups at the surface [1] which is connected with a corresponding increase of the O+N/C ratio near the surface [16], and the formation of charged surface states [4].

5. Conclusions

The plasma-surface interactions were studied for polyimide polymers using low pressure discharges in two gases, N_2O or NH_3, with the main emphasis on moisture uptake. Surface restructuring including opening of benzene rings and breaking of carbonyl and imide groups, has been demonstrated.

Acknowledgments

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