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Plasmon-Like Collective Effects in the Tma-Oda Conductive Layer Obtained by Ion Irradiation

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PLASMON-LIKE COLLECTIVE EFFECTS IN THE TMA-ODA CONDUCTIVE LAYER OBTAINED BY ION IRRADIATION

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ABSTRACT

We show by SIMS analysis that the conductive layer obtained by ion bombardment of TMA-ODA in the 100 keV energy range is in fact constitued of two sheets. The first one results from the accumulation of non volatile compounds, probably arranged in a conjugated dienes structure. Because the physical stage of bond breaks concerns only the linkages with the highest ionization potentials, we can assume, for the energy tranfer between the moving ion and the macro-molecule, a coherent coupling mode (plasmon) defined by $\Omega_{res}^2 = \omega_p^2 + < \omega_{k0}^2 >$ where ω_p is the bulk plasma frequency and $< \omega_{k0}^2 >^{1/2}$ the root-mean-square value of the individual transition frequencies of the concerned valence electrons (i.e. σ and π electrons).

INTRODUCTION

It was observed that radiations, and more particulary ion bombardment, lead important physical and chemical modifications in the whole series of polyimides. Several authors (1, 2, 3, 4) have notably reported an increasing of electrical conductivity from 10^{-16} up to 3.10^2 $(\Omega.cm)^{-1}$. This property made polyimides very interesting as supple conductors. The proposed study lies in this scope.

We have already analysed the conductivity of a particular polyamide-imide (PAI), Trimellitic anhydride-oxydianaline (TMA-ODA) (5), and correlated this one with a shrinkage effect. We complete here this study. Before we start on the subject, we have to be clear about the method used to found a connection between the ion beam-induced physical and chemical modifications and the change observed in the physical and chemical properties of the bombarded solids. With this aim, we distinguish three main reactions types (5) : 1) - The first kind reactions, that can themselves be broken into two parts : their first stage (a1) as resulting from the ion-matter physical interactions (≈ 10^{-15} s) (6) and their second stage (a2), where the highly reactive precursors, formed in the first stage, combine together by physico-chemical processes (≈10^{-10} s). 2) - The second kind reactions (b) that are exclusively chemical type ones.

SHELVED QUESTIONS

TMA-ODA used is produced by Ciba-Geigy Corp. with the trade name Probimide 32. Its formula is drawn in Figure 1.

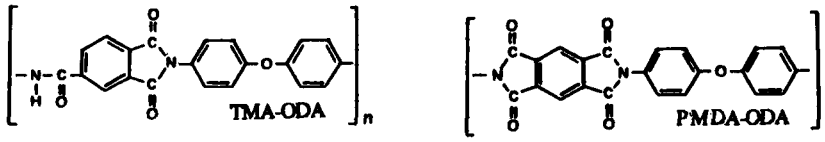

Figure 1 : Chemical formula of (TMA-ODA) compared with that of (PMDA-ODA).

We have assumed an in our previous study (5) ablative developpment of TMA-ODA ("top-down model" : volatilization layer by layer) by the ion beam, with a predominant role of the electronic stopping power. The main processes, that is to say : decarboxylization and elimination of imidic and amidic fonctions, lead to the formation of a conjugated dienes structure able to explain the production of significant conductivity under a layer thickness equal to (Rp + ΔRp) (the mean projected range of the ion and its straggling). As for electroactive polymers, the resistivity reaches a minimum value (9). It occurs when shrinkage saturates for an ion fluence threshold Φ_s dependent on the ion mass, in conformity with results of self-developping resists (9). We have not found justification concerning the remaining CO_2 at the end of the second kind reactions only above the threshold, while a like-isonitrile group disappears. We have neither understood the great number of H_2 molecules evolved, nor that HCN is still produced beyond the threshold. The significance of this last one is unknown. On top of all that, what are the physical reasons that determine the breaked bonds, while others are not damaged ?

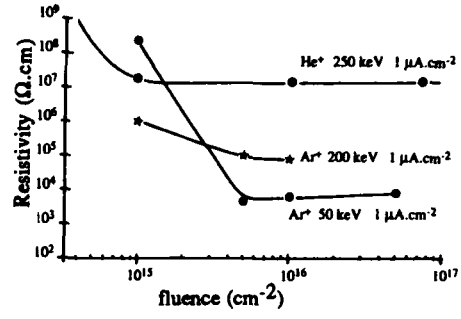

Figure 2 : TMA-ODA resistivity vs fluence for 50 and 200 kev A^+ beam and for 250 keV He^+ beam with a constant current density of 1 $\mu A.cm^{-2}$.

NEW RESULTS AND DISCUSSION

Experimental and results

The samples are obtained by spinning TMA-ODA with a 320 nm thickness. Boron ions of 60 keV are implanted with a constant fluence rate of $6{,}25.10^{11}$ $cm^{-2}.s^{-1}$ (Rp = 268,7 nm ; ΔRp = 49,5 nm (8)). The study versus the ion-fluence is carried out in order to draw the concentration profiles of C and N atoms. These profiles are recorded with a CAMECA SIMS probe, at the end of the second kind reactions. Figure 3 shows a typical recording, obtained in this case with a $1.40.10^{14}$ cm^{-2} ion fluence,

distinctly weaker than the fluence threshold. The major observation is that the remaining layer of TMA-ODA is not homogeneous. A surface sheet of 132 nm thick is created, with C and N atomic concentrations enhancement. The concentration of boron atoms is there less than 10^{18} cm^{-3}. The immediate conclusion is that our previous FTIR analyses, as they are obtained by transmission, have provided results with an average effect over the two different thin layers. Then, the real conductivity values are higher than the previously calculated ones, considering (Rp + ΔRp) as the conduction layer thickness.

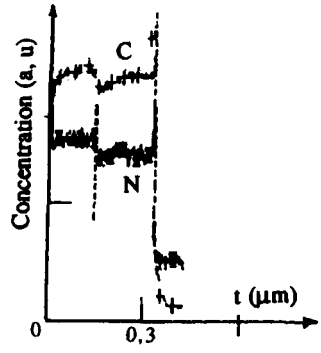

Figure 3 : SIMS profiles of C and N atoms in the remaining bombarded TMA-ODA layer (initial thickness : 320 nm).

Discussion

The first shelved question concerns the presence of CO_2 at the second kind reactions level (b) when the ion fluence is above the threshold, while it disappears below. Marletta (2) has noted, with polyimide derivative BTDA-ODA, an increasing of the atomic concentrations ratios C/N and C/O versus the fluence. Although we observe a nitrogen increasing, these two results are compatible because the trend in density increases. So the existence of CO_2 should be explained by the two next ways.

a - As carbon atoms present near the surface are in an excited state, they react easily with ambiant oxygen to form CO_2. This assumption is often kept in memory. It's built on the Momose's work (10), which proved that PAI are more oxidized than PMDA-ODA by ambiant photodegradation.

b - CO_2 molecules, formed along the ion track by an electronic process during the first stage of the first kind reactions (step a1), as depicted in the next paragraph, migrate from the core of the polymer to its surface. As long as the fluence is below the threshold, they can volatilize at the second stage of the first kind reactions (step a2). But, as soon as the thin carbonaceous conducting layer is formed, that is to say when the threshold is passed, CO_2 will be trapped under this sheet.

If the first assumption is correct, we would find CO_2 below the threshold at the second stage of the first kind reactions (step a2) as well as for the second kind reactions (step b). On top of that, CO_2 IR-bands would increase between these two steps. Neither one nor the other of these facts occurs. This assumption is invalid. We have to note there is no oxydation with the ambiant oxygen. It's consistent with the achievement of a good conduction level.

In opposition, by the means of the second assumption, the trapping of CO_2 above the threshold can be justified. For the second kind reactions (step b), we can explain the vanishing of the like-isonitrile structure. As the fluence increases, the carbonaceous surface sheet becomes more and more dense up to the threshold. When it's reached, the like-isonitrile structure will react with the ambiant air to produce HCN that is sufficiently small to make one's way through the sheet, while CO_2, that is a bigger

molecule, will be trapped. The ion fluence threshold will then take its all significance : when it's reached all the polymer surface is covered by the individual ion tracks. When using the simplified, but very realistic, model of damage tube for the ion track, the diameter of this later will then be equal to : $d = 2\,(\pi\Phi_s)^{-1/2}$. We deduce d = 1.6 Å for He^+ (250 keV) and d = 11.2 Å for A^+ (200 keV). This damaging model implies a shrinkage mechanism by an electronic process into the whole depth equal to the ion projected range. So it invalidates the "top-down model". We can, by this way, also understand why HCN emission, observed by SIMS during the ion bombardment, persists beyond the ion fluence threshold, while the one concerning CO_2 stops.

MODEL OF ENERGY TRANSFER BY PLASMON MODE

Theory

Among electronic interactions, distant collisions are coherent excitations of target elecrons, which initially resonate following adiabatically the long-range electric field of the moving ion. Plasmons, borrowed from Langmuir's description of gaseous plasmas, refer to excitations of a many-electron system characteristic of the electron-density oscillations. In condensed media, because of the the many-body coupling, the valence electrons do not resonate at each individual transition frequency ω_{k0}, but at a higher value Ω_{res} given by (11) : $\Omega_{res}^2 = \omega_p^2 + <\omega_{k0}^2>$ where $<\omega_{k0}^2>^{1/2}$ is the root mean square value of the ω_{k0}, and ω_p the bulk plasma frequency. The collective electron motion leaves holes, which explain the nature of p type condution. The molecular bonds act as localized "resonators". Absording coherently the energy proffered to them by the collective excitations, they dampen the phenomenon by incoherent scattering processes. The quantity of localized transfered energy is determined by the coupling between the absorber and the collective excitation field. Because Ω_{res} is always shifted above ω_p, that is itself higher than each ω_{k0} frequency, the more damaged bonds will be those characterized by the higher ionization potentials. The selectivity will be given by the overlap of the absorption in the continuum g (ω) above the ionization limit of each bond with the distribution in frequency for the collective excitation I (ω). The efficiency of the energy transfer, and hence the quantity of damaged bonds, depends on the magnitude of g_k (ω) at Ω_{res}.

Application to TMA-ODA

TMA-ODA presents a weak conjugated structure. Then we must be interested in the valence-band density of states (VBDOS). This last is not known for TMA-ODA, but has been determined in the case of polymide PMDA-ODA (12, 13). We are not much mistaken considering that of PMDA-ODA instead of TMA-ODA. The observation of the ESCA valence bands of BTDA-ODA (2), which is similar to that of PMDA-ODA, confirms this assumption. Above 16 eV, VBDOS of PMDA-ODA is reported in Figure 4. In comparison with the Kowalczyk's results (12) concerning gaseous state, we have made a shift of 2.3 eV wich is classically observed between solid and gaseous state. The main features appear at 11.2 eV, and include extended states, oxygen lone-pair states and a few π states. The high-binding

energy peak of weak magnitude at 15.4 eV arises from extented 2pσ states. The peak at 8.7 eV is dominated by oxygen contributions. In the low-binding-energy side the peak at 7.1 eV is due to the nitrogen lone-pair states mixed with the p_z atomic orbitals of oxygen. The extended π states of phenyl nucleus characterizes the peak at 5.6 eV. Computing ω_p by the relationship : $\omega_p = (4\pi\rho_e q^2/m_e \cdot \sum_{k}^{val} f_{k0}$, where ρ_e is the eletron density, f_{k0} the oscillator strength at the frequency ω_{k0} (in fact the number of σ and π electrons of each bond k), we find ω_p = 19.15 eV. Taking into account the relative magnitude of each peak of the VBDOS, $<\omega_{k0}^2>$ is equal to112.47 $(eV)^2$. So we obtain : Ω_{res} = 22.19 eV. The validity of the method is proved when applyind it to BTDA-ODA. We find Ω_{res} = 21.84 eV, as the experimental value obtained by REELS technique (2) is 22.0 ± 0.4 eV. Then we see that the main participations to the collective oscillation around the resonant frequency Ω_{res}= 22.19 eV are, from the more important to the less, due to the peaks at 11.2 eV, 8.7 eV, and besides 7.1 eV. Taking into account the origin of these peaks, we understand why during the ion bombardment the more damaged bondings succesively are C - O, C - H, C = O and C - N. By this way the intense production of H_2, the decarboxilization, and the emission of N_2 en HCN are explained.

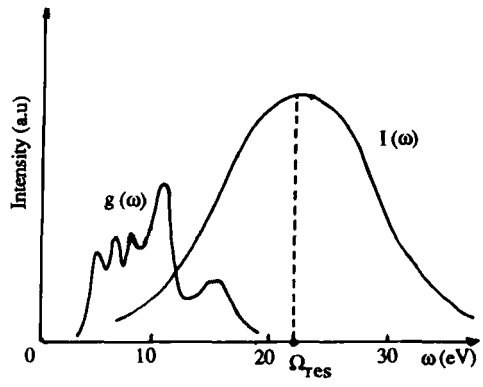

Figure 4 : Overlap of the intensity distribution for the collective excitation I (ω) peaked at Ω_{res} with the VBDOS of PMDA-ODA used as continuum spectra g (ω) of localized bonds of TMA-ODA (the shape of I (ω) is arbitrarily drawn).

CONCLUSION

It seems clearly that plasmon-like collective effects occur in TMA-ODA, and probably in other polyimide derivatives, during ion bombardment in the 100 keV energy range. This phenomenon governs the selectivity of damaged bonds by the means of distant electronic collisions, and justify the p-type of conductivity obtained.

So, it appears that electronic stopping power dominates the energy transfer when the ion is slowing down, as it happens for electroactive polymers dopping (8, 14). The role of the nuclear sropping power has to be elucidated.

With the help of the actual knowledge, the electronic and geometric structure of the surface conductive sheet cannot be determined seriousely. If we are now sure that its thickness is less than the ion projected range, and that this sheet is rich in carbon and nitrogen atoms, the geometric layout is unknown. Similarly, if we know that the relatively high density of localized electronic states is created near Fermi level with a poor mobility (1, 14), we have no information concerning the origin of these states. The

presence of Boron at concentration around 10^{18} cm^{-3}, that is a typical doping concentration for semi conductors, must not be neglected in the discussion. More investigations at the atomic scale are needed.

Acknowledgements

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