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Comparative Study between Wet and Dry Etching of Poly(*N*-vinylcarbazole)

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Summary: This work presents the study of two etching techniques, also applied in polymer. The chosen polymer was poly (N-vinylcarbazole) (PVK), because of its easy processability and custom of process. The polymer was synthesized by ‘‘living’’ free radical polymerization process. Previous studies on the best technique for film preparation had been made. The photolithography process was done, then in sequence the etching process was applied in two separate steps: the wet etching with a polymer solvent and dry etching with argon and oxygen plasma. The comparison of the results shows a significant difference between the etching methods, which will be suitable for films preparation in aiming at novel electronic devices.

Keywords: conductor trails; etching process; poly(*N*-vinylcarbazole)

Introduction

After the discovery of conducting polymers, they have been successfully applied in many kinds of electronic related products due to its ease manipulation. Some of the advantages of the technology development with polymer are the low cost, high processability and handling means. Recently, research on the substitution of inorganic materials by polymeric ones has enlarged. The use of polymer in microelectronic applications is increasing more and more. This work is focused on the study of conducting trails, aiming for the development of a completely polymer based device. Currently, a lot of researches are applying plasma in polymer processing, especially, dealing with polymeric surface treatment by plasma, in order to maximize some properties, as adherence and doping.[1,2]

Recently, we have shown the possibility of PVK etching using plasma, which effectiveness was dependent on the initial film thickness.[2,10]

The use of polymer in microelectronic applications is increasing each more. This work is focused on the study of trails, aiming the development of a device completely based on polymeric material.

Poly(N-vinylcarbazole) (PVK) is well known as an electroactive material due to its good photoconductivity, charge-transfer complexes, photoluminescence and electroluminescence properties, with good thermal and chemical stability.[7–9,12]

Thus, the chosen polymers were the PVK (‘‘living’’ free radical polymerization process) and the photoresist AZ1518.

Experimental

Synthesis of Poly (N-vinylcarbazole)[3] Currently, the electrochemical process is the most used one in the polymerization of the PVK. But, in this work, it was used the free radical polymerization process, in order to confirm the method efficiency proposed by Possidonio.[3] For the synthesis

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of the polymer, biomolecular initiators BPO and TEMPO were used. The monomer (N-vilnylcarbazole) was recrystallized two times. A fraction of the monomer and the initiators were placed in a test tube and then introduced into a silicone oil bath during 141 hours. A temperature of 130 °C was kept, since the initiator BPO reacts at 60 °C and the TEMPO at 130 °C (Figure 1).

The white solid resulted from the polymerization was dissolved in chloroform and, in sequence, seven parts of the methanol, by volume (non solvent of PVK), were added to the solutions in order to recover the purified solid polymer.

Film Deposition

For the manufacture of the film two techniques could be used: casting or spin coating. In the casting method the obtained film did not presented the adequate homogeneity. By spin coating process it was possible to control the thickness and to prepare good coated glass substrates.

Good quality film was prepared by using an optimized mass of polymer dissolved in chloroform (5% wt), which was then poured on a glass plate slowly during 30 s at 2000 rpm (spin coating method).[5]

The polymer was dissolved in this percentage in mass, because in previous tests it was noticed that the solution viscosity has a strong influence in the film homogeneity. For concentrations lower than 5 wt%, the liquid films spread just a little, while in higher concentrations, problems with solubility were observed and the films became dried during the spin coating process.

A remarkable point is that solutions with concentration higher than 5 wt% are very viscous, providing non-homogeneous films. While for concentrations lower than 5%wt, the obtained films are very thin.[2,5]

The initial thickness of the film was of 3.651 μm.

Photolithography Process

Mechanical metallic masks had been used at the beginning of the study, however degradation of the polymeric film was observed, which could be explained by Foucault's chain phenomenon, that provoked intense heating in the film and degradation. A rectangular geometry 2 mm × 22 mm, 1 mm spaced was used. The photolithograph process was used for the protection of the areas of the PVK film. The photoresiste used was AZ1518, and a conventional photolithograph process was followed.[5,13]

Etching Process

For the usual photolithograph[5] process, acetone is used for the photoresist removal, however studies proved that PVK is not soluble in acetone.[3]

Although, the chloroform is a good solvent for PVK, it attacks the photoresist. Thus, some tests on polymer solubility for

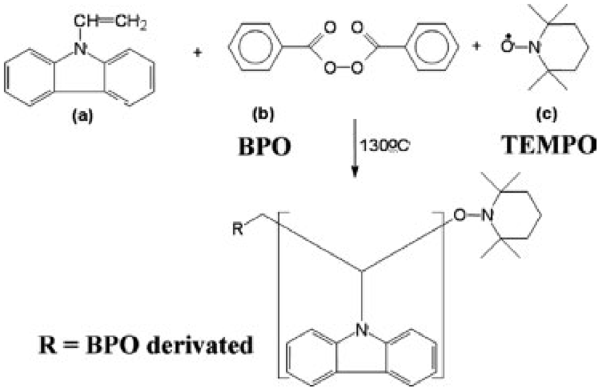

Figure 1.
Scheme of the synthesis of (a) N-vinylcarbazol homopolymer using (b) BPO and (c) TEMPO as initiators by a free radical polymerization process.

Figure 2.
Plasma RIE equipment from Plasma Technology, model: Plasma Lab TTL.

both, PVK and photoresist, were done. The best solvent found for PVK was toluene, which also assured the integrity of the photoresist.

Argon plasma was used in the dry etching method. According to previous works,[4,10,11] the dry etching with argon plasma is effective for PVK corrosion. The substrate containing the polymeric film was placed on the active electrode and the discharge was obtained with DC high voltage. The camera has a 12 cm diameter disk and it is fed by rectifying voltage from the output of the secondary generated by a step voltage transformer. The power control is accomplished at the entrance of the transformer.[6] The vacuum system is served by one turbo molecular and one mechanical pump. Between the turbo molecular pump and the evacuated chamber, exists a drawer valve. During the deposition, that drawer valve is set at the minimum flow and the pressure of the system is controlled by the argon flux. The oxygen plasma RIE (Figure 2) is outlined in Figure 1. The conditions for the plasma production were: 100 W RF power, 20 sccm of gas flow, 100 mTorr of pressure and 4 minutes of attack time.

Results and Discussion

Tests with the photoresist, the polymers and solvents.

It was found that there is a trade off between the suitable solvent for the obtained PVK and the photoresist.

In spite of being easily removed by acetone, the photoresist is not attached by toluene.

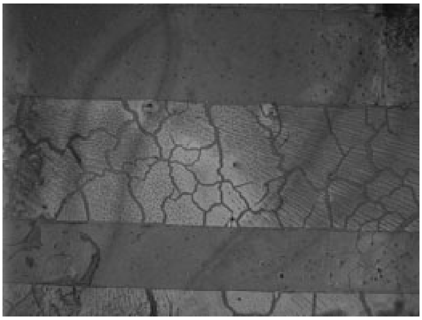

Figure 3.
Wet etching, optical microscope 22.5×.

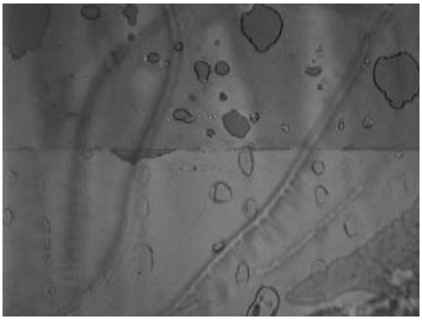

Figure 4.
Limits in the etching. Optical microscope 500×.

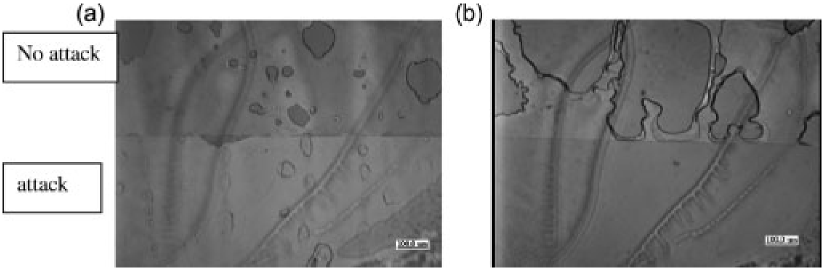

Figure 5.
Optical microscope 500× (a) argon etching (b) oxygen etching.

Meanwhile, toluene can remove the PVK films in short time.

The trails were obtained with some fissures (Figure 3). The observed thickness were not suitable for conductor trails, purpose of this work. Another aspect is that some of these fissures traversed the trails resulting in interruptions.

Plasma of argon

The conditions of the plasma were set at $2 \cdot 10^{-1}$ mbar of pressure, 0,84 W/cm^2 of power in order to avoid significant temperature elevation. The plasma performed for 2 minutes, which did not allow total removal of the non-protected region. On the other hand the etching rate in those conditions could be measured, 1.180 μm/min without photoresist protection. The obtained trails are better than those ones resulting from the wet etching. The limits, presenting well-defined borders as shown in Figure 4.

Plasma Oxygen

The oxygen plasma attacks PVK, leads to superior trail quality compared to the argon plasma.[4] Previous studies show that the trails obtained from argon plasma are well-defined, but in this study even better defined trails were verified (Figure 5).

The film was exposed to the oxygen plasma. The oxygen plasma was produced at 100 W, under O_2 flow of 20 sccm and pressure of 100 mTorr at 20 °C temperature. After the plasma treatment, the thickness was determined by an ALPHA STEP 500 profile-o-meter. The polymer trail sizes were around 2 mm wide and 20 mm length.

The result of the plasma etching is shown in Figure 6. It was possible to check the corrosion uniformity up to 2 min. of plasma

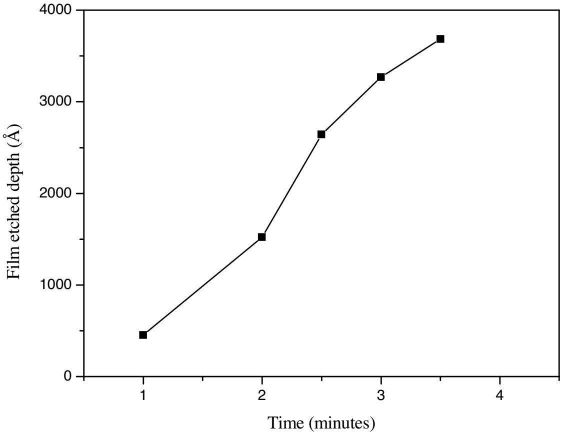

Figure 6.
Film etched depth in function of plasma treatment time.

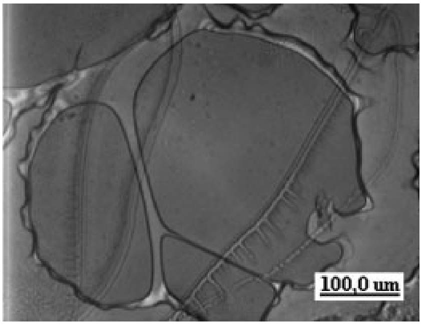

Figure 7.
Optical microscope 1000× (argon etching).

attack. Longer time provoked an initial saturation leading to thickness variation along the film. Surprisingly, the photoresist was not etched by the oxygen plasma. The initial results indicate the possibility of achieve uniform thin conducting films by adjusting plasma treatment parameters.

However, in the present conditions, the prepared trails are not appropriate for the proposed function. The reason is the nucleation phenomenon, which is very intense. Interruptions in the trails can possibly occur, breaking the electronic conduction (Figure 7). This phenomenon occurs in the plasma argon process.

Conclusion

In the wet etching the polymer presented more stresses than in the dry etching. The fissure thicknesses can damage the circuit of the conductor trails, as shown in Figure 1.

The definition of the trails in the dry etching method is much better, presenting reliability for the purpose of this study, which is to develop conductive trails for the application in devices.

The dry etching rate is good, since it can be controlled, differently from the wet etching method. In the latter, the non-protected region is removed instantly. New studies can verify the limit of the widths of these trails, and their conformity for the application ends in electronic devices.

The oxygen plasma is able to etch the poly (N-vinylcarbazole), obtaining well-limited trails. The corrosion rate in the oxygen plasma case is greater than that in the argon plasma. The argon plasma decreases the initial thickness of the trails, is able to harm the electronic performance of the same ones, what apparently does not happen with the oxygen plasma method. New plasma parameters conditions should be studied, in order to get the wanted trails.

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