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M. Angelopoulos [a] , J. M. Shaw [a] , W.-S. Huang [b] & R. D. Kaplan [b]

[a] IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York, 10598

[b] IBM Corporation, General Technology Division, East Fishkill, New York, 12533

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In-Situ Radiation Induced Doping

M. ANGELOPOULOS and J. M. SHAW
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

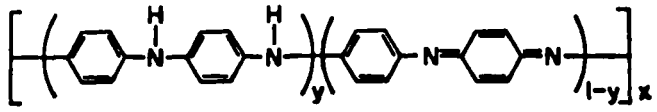
and

W.-S. HUANG and R. D. KAPLAN
IBM Corporation, General Technology Division, East Fishkill, New York 12533

In this paper we describe a novel method of inducing conductivity in polyaniline photochemically or by electron-beam exposure. This is accomplished with the use of onium salts which are a class of materials that decompose upon irradiation generating protonic acids. We find that the onium salt may be blended with the polyaniline and upon irradiation, the generated acid acts as an in situ dopant for the polymer. Conductivity on the order of $\simeq 0.1$ S/cm has been attained. This system has significant applications in lithography since it allows patterns of conducting lines to be generated. The polyaniline/onium system represents the first electrically conducting photo and electron-beam resist. In addition, we find that this radiation induced doping technique is applicable to polythiophene systems as well.

I. INTRODUCTION

A great deal of attention has recently been focused on the polyaniline[1–8] class of conducting polymers whose chemical composition in the non-conducting or base form is as follows.



Entirely new scientific concepts[1–8] as well as potential for technological applications[9–10] have emerged with these materials.

The emeraldine oxidation state of polyaniline (y = 0.5 in the above equation) in its non-conducting or base form "emeraldine base" has been the most widely studied of the polyaniline materials. It is solution processible from both organic and aqueous solvents.[11–12] It has been found to undergo an insulator to metal transition upon doping with cationic reagents most commonly protonic acids to

yield the metallic emeraldine salt whose maximum conductivity is ≃5 S/cm.[3,4] The doping process has generally involved reacting the emeraldine base in either a powder or film form heterogeneously with a dopant solution.[3,11,12] Alternatively, the doping process has been accomplished homogeneously be reacting a solution of the emeraldine base in an appropriate solvent, e.g. N-methylpyrrolidinone (NMP) with a solution of the dopant.[13] In this paper we report on a new doping method for emeraldine base in which the conductivity is induced by radiation with the use of onium salts.

Crivello and Lam[14,15] have previously shown that triarylsulfonium and diaryliodonium salts decompose upon ultraviolet irradiation to generate protonic acids. These salts have been used to photochemically dope the non-soluble polyacetylene[16] and polypyrrole[17] by dipping films of the material into a solution of the onium salt and subsequently exposing the films to ultraviolet radiation. In these systems, the onium salts are impregnated into the polymer films. Polyaniline, being solution processible, offers the advantage that the material can be uniformly blended in solution with the onium salt.

In this report we will first describe the radiation induced doping for polyaniline (emeraldine base) and present experimental results for the transition to a conducting state upon irradiation. In addition, the application of this system as a resist material in lithography will be discussed. Finally, the extension of the doping method to soluble poly-alkylthiophenes will be presented.

II. EXPERIMENTAL

Polyaniline was synthesized as previously described.[18] The emeraldine base form of polyaniline was dissolved in N-methylpyrrolidinone (NMP) and the solution was subsequently filtered through a 0.2 μm micropore filter. The onium salt (triphenylsulfonium hexafluoroantimonate) was also dissolved in NMP. Different amounts of the onium salt were used ranging from a 10 mole percent to the full stochiometric value. The dissolved NMP solution of the onium salt was then added to the polyaniline solution and allowed to stir for ≃15 minutes. The resulting two component solution was used to spin coat films on quartz and silicon wafers.

The samples were exposed to ultraviolet radiation through a narrow band filter at 240 nm or to an electron-beam (e-beam) system. In one experiment the optical spectrum of the polyaniline/onium salt system was monitored before and after different doses of exposure in the same film. Conductivities were measured with a 4-probe instrument.

III. RESULTS AND DISCUSSION

Radiation Induced Doping in Polyaniline

When a film of the polyaniline/onium salt system is exposed to ultraviolet radiation, the polyaniline becomes conducting. The acid which is generated by the radiation induced decomposition of the onium salt acts as an in situ dopant for the polymer.

Visually, one can observe a color change in the film. Prior to exposure, the polyaniline/onium film is blue which is the characteristic color of the non-conducting form of the material. Upon exposure, the film becomes green characteristic of the conducting, i.e. doped form of the polyaniline.

Optical absorption spectra for a polyaniline/onium film before and after different doses of exposure are given in Figure 1. The unexposed film displays two absorption peaks at 2 eV and 4.1 eV. These peaks have been extensively reported for the non-conducting emeraldine base.[7,8] The 2 eV peak is associated with the formation of an exciton based on charge transfer between the aromatic benzenoid and the quinoid-type rings found in the emeraldine base structure. The 4.1 eV peak is the bandgap associated with the polymer. Upon exposure to ultraviolet radiation, dramatic changes are seen in the optical absorption spectrum of the polyaniline/onium film. The 2 eV peak decreases with increasing exposure dose and two new peaks appearing at 1.5 eV and 2.8 eV increase with increasing exposure dose. These peaks have been previously associated with the conducting, i.e. doped emeraldine salt and are believed to arise from excitations to the polaron band.[7,8] The optical absorption data clearly illustrate the transition from the insulating emeraldine base to the doped, conducting emeraldine salt upon exposure to ultraviolet radiation. The last scan in Figure 1 corresponds to a dose of 300 mJ/cm.^{2} However, a significant change in the absorption spectrum was evident after the first exposure dose of 100 mJ/cm.^{2}

This method of inducing doping in polyaniline does not require any external dopant solutions as do the previous doping techniques. In this method, the dopant is generated "in situ." The conductivity of the polyaniline/onium system is, of course, a function of the amount of onium salt used and exposure dose. Conductivity on the order of $\simeq$0.1 S/cm was attained with the polyaniline/triphenylsulfonium hexafluoroantimonate system. The doping process with the onium salts was also found to occur smoothly upon e-beam irradiation.

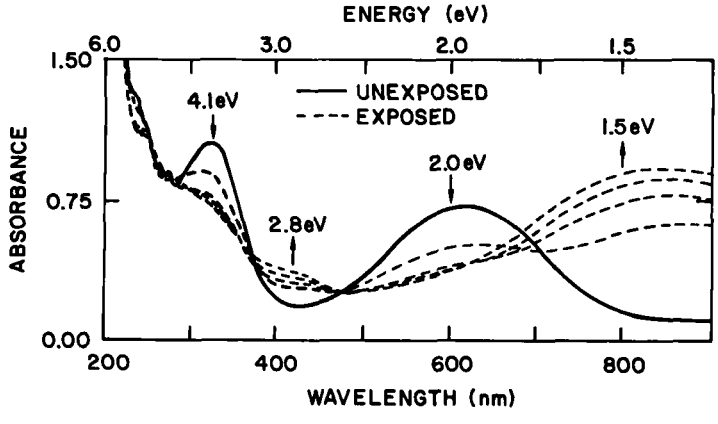


FIGURE 1 Optical Absorption Spectra for the Polyaniline/Onium System before (Solid Line) and After Different Doses of Exposure (Dotted Line). The Same Film was Used for all the Scans. The Exposure Dose was Increased From 100 (First Scan) to 175 to 225 to 300 mJ/cm^2 (Last Scan).

Applications in Lithography

The polyaniline/onium system may have significant applications in the area of lithography as a resist system. Resists are materials in which irradiation creates a solubility difference between the exposed and unexposed regions thereby, allowing patterns to be generated. The exposed regions of the polyaniline/onium film become doped and thus, insoluble whereas, the unexposed regions are readily dissolved in organic solvents. If the polyaniline/onium film is exposed through a mask, the unexposed regions can subsequently be removed by an NMP wash and thus generate conducting patterns. We have, therefore, developed a novel conducting photo and e-beam resist with polyaniline using the photochemical and e-beam induced doping technique. Conducting lines on the order of 0.5 μm have been attained.[19] The previous studies on the photochemical doping of polyacetylene and polypyrrole did not result in resist systems since the exposed and unexposed regions of the film were both insoluble.

Radiation Induced Doping in Polyalkylthiophenes

More recently, we have found that the doping method discussed above for polyaniline is applicable to polyalkylthiophenes. When a film of poly(3-butylthiophene) and triphenylsulfonium hexafluoroantimonate is exposed to either ultraviolet radiation or e-beam, the polythiophene derivative becomes doped. Although the process has yet not been optimized, conductivities in the range of $\simeq$0.02 S/cm have been attained. Further details on this system will be provided in a subsequent report.

IV. SUMMARY

We have shown that onium salts which generate acid upon irradiation can be used as in situ dopants for the polyaniline. The polyaniline and the onium salt can be uniformally blended in solution and subsequently films can be attained. Upon exposure to ultraviolet radiation or e-beam, the polyaniline is converted to the doped conducting form. This doping technique eliminates the need for external dopant solutions which have commonly been used in the previous methods of doping polyaniline.

Upon irradiation of the polyaniline/onium system, a solubility difference is created between the unexposed (non-doped) and exposed (doped) regions and thus, patterns of conducting lines can be generated. The polyaniline/onium system represents the first electrically conducting photo and e-beam resist. We have also demonstrated this radiation induced doping method on polythiophene materials.

References

1. T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electranal. Chem.*, **161**, 419 (1984).
2. E. J. Paul, A. J. Ricco and M. S. Wrighton, *J. Phys. Chem.*, **89**, 1441 (1985).
3. J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986).

4. A. G. MacDiarmid, J. C. Chiang, A. F. Richter and A. J. Epstein, *Synth. Met.*, **18**, 285 (1987).
5. A. J. Epstein, J. M. Ginder, F. Zuo, H. S. Woo, D. B. Tanner, A. F. Richter, M. Angelopoulos, W. S. Huang and A. G. MacDiarmid, *Synth. Met.*, **21**, 63 (1987).
6. F. Zuo, M. Angelopoulos, A. G. MacDiarmid and A. J. Epstein, *Phys. Rev. B.*, **36**, 6 (1987).
7. S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid, *Phys. Rev. Lett.*, **59**, 13 (1987).
8. A. J. Epstein and A. G. MacDiarmid, *J. Mol. Elect.*, **4**, 161 (1988).
9. A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, *Mol. Cryst. Liq. Cryst.*, **121**, 187 (1985).
10. T. Kobayashi, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.*, **161**, 419 (1984).
11. M. Angelopoulos, A. Ray, A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, **21**, 21 (1987).
12. M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr and A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, **160**, 151 (1988).
13. M. Angelopoulos, S. P. Ermer, S. K. Manohar and A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, **160**, 223 (1988).
14. J. V. Crivello and J. H. W. Lam, *Macromolec.*, **10**, 1307 (1977).
15. J. V. Crivello and J. H. W. Lam, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 977 (1979).
16. T. C. Clarke, M. T. Krounbi, V. Y. Lee and G. B. Street, *J. Chem. Soc., Chem. Commun.*, **8**, 384 (1981).
17. S. Pitchumani and F. Willig, *J. Chem. Soc., Chem. Commun.*, **13**, 809 (1983).
18. A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri and A. J. Epstein in *Conducting Polymers*, edited by L. Alcacer, Reidel Publications, Dordrecht, Holland 105 (1985).
19. M. Angelopoulos, J. M. Shaw, W. S. Huang and R. Kaplan, manuscript in preparation.