STRUCTURAL, ELECTRONIC AND OPTICAL EHAVIOUR OF OLUTION-GROWN POLYVINYLCHLORIDE (PVC) FILMS

by

ALOK C. RASTOGI
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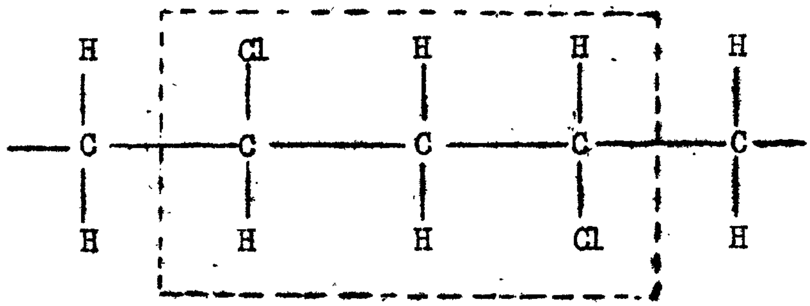
Thin Films of both organic and inorganic insulating materials have been the subject of extensive studies[1-6] in recent years due to their possible applications in capacitors and for insulation, protection and passivation in microelectronics. Thin films of inorganic materials, in particular inorganic oxides, are generally prepared by thermal evaporation, sputtering, chemical vapour deposition and anodization. In these techniques, the basic process of growth in the early stage of a thin film via discrete nucleation centres results, directly or indirectly, in the occurrence of microscopic pinholes or voids. These pinholes are often the significant sites of dielectric breakdown and gaseous diffusion from the ambient. By properly choosing the deposition parameters, it is possible to minimize, although not to eliminate, the pinhole density in comparatively thick (>1000 A°) films. Further, the process of condensation produces enormous ($\sim 10^9-10^{10}$ dyn/cm^2) stresses in the inorganic dielectric films[1]. These stresses in some cases may drastically change their magnitude and even their sign on exposure to water vapour and reactive ambient gases. Therefore, crazing of thick films is a familiar, although undesirable, phenomenon. The problem of pinholes and stress-induced crazing in inorganic dielectric films can be largely overcome in thin films of polymers of organic materials having a long and flexible chain-like structure. In addition to their negligible electrical conductivity, small dissipation factor and high dielectric breakdown strength, a number of polymers are known[7] to be inert to moisture and ambient gases and also to be thermally stable over as large a temperature range as -100 to +200°C. Long chain hydrocarbons also possess many of the useful characteristics of polymers but they are generally not thermally stable at temperatures much above room temperature and thus are not well suited for applications. Clearly, therefore, polymers are attractive material to study in thin film form. The interest is further stimulated by the possibility of preparing a new class of materials in the form of polymer films containing metal atoms and charge transfer or donor-acceptor complexes, as indicated by the successful preparation of a limited number of metallo-polymers in bulk[8].

Polymer films of various polymers, e.g. polyoxymethylene, polypropylene and polystyrene have been obtained[9,10] by the simple technique of direct isothermal immersion of a substrate into a suitable solution of the polymer and also by allowing the evaporation of the solvent from the polymer solution placed on the substrate. The former technique of solution growth appears to be most promising for obtaining reliable and useful thick polymer films. However, with the exception of limited electronmicroscopic studies of epitaxial growth of a few polymer films, neither the deposition conditions, kinetics of growth and structural details, nor the dielectric (or any other) properties of such films have so far been investigated.

In view of the preceding remarks, we have undertaken, for the present thesis, a detailed study of the polyvinylchloride (PVC) films grown from the solution. PVC was chosen because it is known to be a good insulator with a low value of loss factor and, therefore, offers good possibilities for applications. Further, its bulk structure is also well known. It polymerizes in syndotactic form as shown below.



The larger molecular weight, the syndotactic nature of the polymer, the polydispersity of molecular forces and large unfolded length of the chains make nucleation, growth and structural studies of PVC films on polar and nonpolar substrates of considerable interest to the understanding of the growth mechanism.

In the present work, the solution growth technique of depositing a film by the isothermal immersion of a substrate in a PVC solution of suitable concentration has been scientifically developed and put on a quantitative basis. Chapter I describes the results of the study of kinetics and mechanism of growth of such films. The salient features of the growth behaviour have been explained in terms of an adsorption controlled multiple nucleation model.

In order to confirm the proposed model for the growth of PVC films, structural investigations of various growth stages of these films on glass, mica and rocksalt substrate were undertaken. Under certain growth conditions, amorphous, mixed amorphous and crystalline and epitaxial growth were observed. Prior to our work, some studies of epitaxial growth of solution grown films of a number of isotactic homopolymers on several alkali halide substrates have been carried out. However, these studies have not been systematically performed to understand the expected influence of the chemical nature, concentration and temperature of the solvent. In view of this discrepancy, a detailed and systematic study of the effect on epitaxial growth of all these parameters which affect the nucleation and growth of the PVC film was undertaken.

We have also studied the crystallization behaviour of amorphous PVC films on annealing. It was found that a metal film deposited on amorphous PVC film induces rapid crystallization of the film. The nature of crystallites produced was found to depend on various parameters.

The study of the structure, the occurrence of epitaxial growth on single crystal substrates and the recrystallization behaviour of amorphous PVC films which have been carried out using electron diffraction, electron and optical microscopy techniques, forms the subject matter of the second Chapter.

In order to obtain information about the dipolar orientation, electron, hole and ion trapping, interchain processes, charge storage phenomenon and formation of charge transfer complexes in solution grown PVC films, dielectric loss and thermally stimulated discharge (TSD) current measurements have been performed on polarized and unpolarized pure and iodine doped PVC films. Dielectric loss behaviour in bulk PVC samples has been reported in the literature. Though motions of molecular chains in the polymer have been shown to contribute to the dielectric loss, the physical nature of these motions as related to the dielectric loss has not received enough attention. Our studies have shown that dielectric loss and TSD current are due to dipolar relaxation process. The results of these investigations are dealt with in Chapter III.

The study of electronic conduction in thin polymer films have attracted a great deal of attention in literature. The mechanism of electrical transport in polymeric materials is very complicated and is related not only to their physical structure, but also to their chemical nature. In this thesis, we have studied the effect of temperature, electric field and frequency on the conductivity of solution grown thin pure and iodine doped PVC films. The results and their interpretation are discussed in Chapter IV.

It has been shown that polymer films generally scatter the visible light. The study of the scattering behaviour can yield useful information regarding the structure of these films. We have, therefore, undertaken the study of angular variation of monochromatic light and wavelength dependence of the transmitted light as a function of PVC film thickness. The results of these studies are described in Chapter V.

The major results of the various studies reported herein are published as follows:

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