Characterization of Thin Ferroelectric Polymer Films by Optical Methods

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Abstract. Ferroelectric polymers are a group of crystalline polar polymers that possess permanent electric polarization that can be controlled by an external electric field. Ferroelectric polymers such as polyvinylidene fluoride (PVDF) and poly (vinylidene fluoride-co-trifluorethylene) (P(VDF/TrFE)), are very attractive for various applications since they have a high piezoelectric and pyroelectric properties and low acoustic impedance, which corresponds to human skin and water. To investigate the ferroelectric properties it is necessary to make the so-called “sandwich”-structures substrate-electrode-polymer-electrode. To improve the quality of the result and reduce production errors, we offer a variety of optical methods for quality control and research, namely spectrophotometry, goniophotometry and ellipsometry.

Introduction

Ferroelectric polymers are a group of crystalline polar polymers that are also ferroelectric, meaning that they maintain a permanent electric polarization that can be reversed, or switched, in an external electric field.

First reported in 1971, ferroelectric polymers are polymer chains that must exhibit ferroelectric behaviour, [Ducharme et al., 2008] and possibly, but not required, piezoelectric behaviour [Lovinger et al., 1983] and pyroelectric behaviour. [Lovinger et al., 1983]

Ferroelectric polymers, such as polyvinylidene fluoride (PVDF), are used in acoustic transducers and electromechanical actuators because of their inherent piezoelectric response, and as heat sensors because of their inherent pyroelectric response. [Lovinger et al., 1983]

In 1969, strong piezoelectricity was observed in PVDF, with the piezoelectric coefficient of poled (placed under a strong electric field to induce a net dipole moment) thin films [Kawai et al., 1979].

PVDF is commonly used as insulation on electrical wires, because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance. The piezoelectric properties of PVDF are used to advantage to manufacture tactile sensor arrays, inexpensive strain gauges and lightweight audio transducers. PVDF is the standard binder material used in the production of composite electrodes for lithium ion batteries. It is used because it is chemically inert over the potential range used and does not react with the electrolyte or lithium. In the biomedical sciences PVDF is used in immunoblotting as an artificial membrane. PVDF transducers have the advantage of being dynamically more suitable for modal testing applications than semi-conductor piezoresistive transducers, and more compliant for structural integration than piezoceramic transducers. For those reasons, the use of PVDF active sensors is a keystone for the development of future structural health monitoring methods, due to their low cost and compliance. [Guzman, E. et al., 2013]

Optical usage of P(VDF/TrFE) is a special interest in development of optoelectronic devices. Polarization plane turn under electric field influence makes polymer interesting for polarimetric application. For investigation of optical properties of ferroelectric polymers special “sandwich”-structures have to be manufactured. Also special non-destructive uninvasive optical methods need to be chosen.

Samples

The liquid polymer solution of P(VDF/TrFE) polymer in organic solvent (DMA) was inflicted on number of glass and Si substrates with spin coating method.
An important consideration when preparing the samples appeared selection of the desired concentration of the polymer powder in an organic solvent solution for the manufacture of a liquid polymer. Highly concentrated polymer gives bulbs on the surface of substrate. In other way if there is not enough polymer in the solution “island” structures appear. The best solution we get is 17 % of P(VDF/TrFE) in organic solvent (DMA). Optical microscopy images are presented in Figure 1.

To get electric field through thin ferroelectric film and investigate its ferroelectric properties “sandwich” structure of the substrate-electrode-polymer-electrode were made. Geometric scheme of sample layers is given in Figure 2. Glass substrate is coated with ITO electrodes (left), then a layer of polymer of given shape (centre) is delivered and top Al electrodes are sputtered (right).

**Spectrophotometry**

As polyvinylidene fluoride polymer (PVDF) often used with doping or copolymers it is necessary to have additional control of molecular structure. Important thing is to make it without destruction of the sample. It can be done by analysing optical transmittance spectra of the films.

P(VDF/TrFE) films have very low absorption in visible range (Figure 3, left). This spectrum was obtained on CΦ-14 spectrophotometer. As polymer found its application in thermal and infrared sensors getting transmittance spectra in IR range becomes important. We can see that in that range (Figure 3, right) there are couple of informative absorbance lines.

Analysing information from spectra of the sample could give us knowledge about composition and structure of solution or final film. In our case we can talk about presence of trfluorethylene copolymer in final composition.
Ellipsometry

Ellipsometry is an optical technique for investigating the dielectric properties (complex refractive index or dielectric function) of thin films. Ellipsometry can be used to characterize composition, roughness, thickness (depth), crystalline nature, doping concentration, electrical conductivity and other material properties. It is very sensitive to the change in the optical response of incident radiation that interacts with the material being investigated.

Every kind of sample needs developing individual model to operate with the main ellipsometry parameters dependences (Figure 4) and get the specified information.

Samples on Si substrates and glass substrates were investigated. In the first case monolayer model gives results but in the second case model has to include more surfaces. Now work on such model is in progress.

Goniophotometry

Since thin P(VDF/TrFE) polymer films have very low absorption coefficients what was confirmed with previous investigations there are some difficulties in using optical investigation methods.

Therefore goniophotometry can give high accuracy results in examining the surface and scattering inside the media. Getting the scattering indicatrix of the sample and analysing it can give us such information. Our self-constructed automated optoelectronic goniophotometric device was used for these purposes.

Angle distribution of scattered light or scattering indicatrix (Figure 5) carries information about surface, inner structure, thickness etc. of the sample. Analysing slope of each branches of indicatrix, recovering highness of the main peak can help obtaining necessary parameters. Secondary peaks are carrying information about scattering centres on the surface or inside the media of the sample.

Future hardware updates will give opportunity to provide polarization measurements and getting Muller matrixes of the sample.

Figure 3. P(VDF/TrFE) transmittance spectrum. Left — visible range, right — IR range.

Figure 4. Main ellipsometry parameters of thin polymer film.
Conclusion

The ferroelectric polymers such as polyvinylidene fluoride with trifluorethylene copolymer P(VDF/TrFE) presented in our work has specific characteristic which make them suitable for different practical purposes. It is widely used in the whole world for manufacturing sensors and parts of optoelectronic devices.

In collaboration with Shizuoka University, Hamamatsu, Japan amount of samples of thin polymer films on glass substrates, Si substrates and “sandwich”-structures were manufactured. A number of uninvasive non-destructive studies that examine the optical properties of the samples as well as useful for quality control of manufactured samples are given.

Spectrophotometry can give information about molecular structure and doping in solvation of the polymer. Infrared region is more important as P(VDF/TrFE) is used for infrared sensing. Spectrum in the range 800–1900 cm\(^{-1}\) for thin ferroelectric films is obtained.

Ellipsometry can give opportunity to investigate surfaces of samples, examine thicknesses and provide polarimetric studies. The multi-layer model is developing to get the main optical constants such as the absorption coefficient and refractive index of samples.

Goniophotometry can give high accuracy results in examining the surface and scattering inside the media. Getting the scattering indicatrix of the sample and analysing it can give us such information.

References

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