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Studies on the nonlinear optical properties of rf plasma polymerized aniline thin films by open aperture *z*-scan technique

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ABSTRACT

Plasma polymerized polyaniline (PANI) thin films in their pristine and iodine doped forms were subjected to open aperture *z*-scan studies in order to investigate the nonlinear optical (NLO) properties of these materials. The investigations were carried out using a Q-switched resonant Nd:YAG laser at a wavelength of 532 nm for various fluences. The *z*-scan studies revealed that RF PANI thin films exhibit a saturable absorption (SA). Iodine doping modifies the NLO characteristics of these films substantially. These results qualify PANI thin films as potential materials for NLO materials. Investigations on the NLO properties of pristine (PANI) and iodine doped polyaniline (dPANI) thin films in its plasma polymerized form are reported for the first time.

1. Introduction

Organic conjugated polymers are of interest in the photonic/opto-electronic research due to their strong electro luminescence (EL), photo refractive (PR) response and nonlinear optical (NLO) properties [1,2]. The NLO materials based on polymers exhibit third order optical nonlinearity at different wavelengths and are promising candidates for applications like optical switching and optical limiting. The NLO properties exhibited by organic conjugated polymers like, poly-phenylene vinylene (PPV), pyridyl para-phenylene (PPP), etc., and inorganic materials like phthalocyanine were investigated by many researchers. From a fundamental point of view, materials exhibiting NLO properties can be categorized into many, depending on the particular mechanism with which they execute when subjected to intense laser radiation [3]. For example, saturable absorption (SA), two photon absorption (TPA) and excited state absorption (ESA) are the most relevant types of nonlinear absorption processes. TPA involves the simultaneous absorption of two photons to excite a material. SA involves the saturation of a given transition, by populating the excited state of the material so that the material, which initially absorbed at that wavelength, becomes more transparent. ESA involves a sequential process in which a photon is initially absorbed and the molecule remains in an excited state of the material so that a second photon that arrives during that time is also absorbed to put the molecule into an even higher excited state [4,5]. *z*-Scan technique is a simple and effective tool to evaluate these properties. It will ascertain the usefulness of a material as a nonlinear optical (NLO) material and also led light in to the mechanism of NLO transition occurring in the material [6,7].

Plasma polymerization is an efficient measure to produce polymer thin films from their monomer precursors. The most commonly employed plasma polymerization techniques to produce polymer thin films are dc, pulsed, ac, rf and microwave [8]. Using this technique pinhole free, homogeneous and thermally stable thin films can be prepared with ease. Moreover *in situ* doping of these films with iodine is possible by admitting controlled or regulated quantity of iodine vapour to the plasma chamber. Such *in situ* doping normally results in stable, doped plasma polymer thin films, unlike in the conventional methods, where vaporization of iodine always results in unstable films. Pristine and iodine doped PANI thin films were synthesized by plasma polymerization technique and have been subjected to various studies recently. Researchers have found that they exhibit low dielectric characteristics and can be a potential low dielectric interlayer dielectric material [9,10]. The photoluminescence properties of PANI thin films have also been reported [11]. Some reports on the NLO properties of PANI thin films

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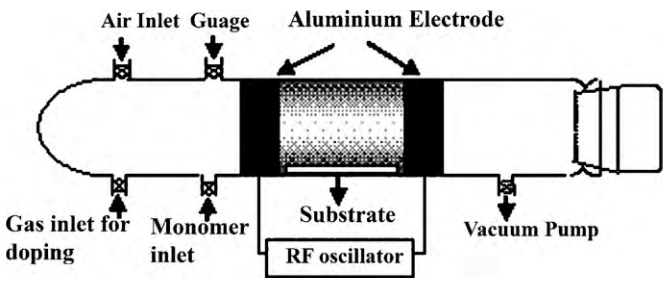

Fig. 1. Setup for rf plasma polymerization.

prepared by chemical methods are already available [12]. However a survey of literature reveals that not much information exists on the NLO properties of PANI thin films. The ellipsometric studies carried out on these films by the authors gave an indication that these materials might exhibit nonlinear optical properties and thus an unexplored and virgin area as far as the NLO properties are concerned [13]. In the present investigation PANI and dPANI thin films are subjected to open aperture *z*-scan studies. Emphasis is laid in understanding the mechanism of nonlinear absorption. The effect of iodine doping on the NLO properties will also be dealt with in this study.

2. Experimental

The experimental setup for the preparation of rf plasma polymerized aniline (PANI) thin films is depicted in Fig. 1. In brief the reaction chamber consists of a long glass tube of length 50 cm and of a diameter around 5 cm with provisions for passing monomer vapour, dopants and for evacuation. Chemically and ultrasonically cleaned glass substrate was placed inside the glass tube exactly under the space separated by the aluminium foil electrodes, which are capacitively coupled and wrapped around the glass tube separated by a distance of 5 cm. The chamber was evacuated and the monomer was passed into the chamber. Glow discharge was obtained in between the electrodes by applying a frequency (13.56 MHz) and an ionic current of 80 mA at a power of 20 W. The doping is carried out *in situ* by admitting iodine vapour in to the chamber in such that the pressure in the chamber is unaffected. In the present study PANI thin films of thickness 320 nm is used for the studies, both for the pristine and iodine doped forms. The fine

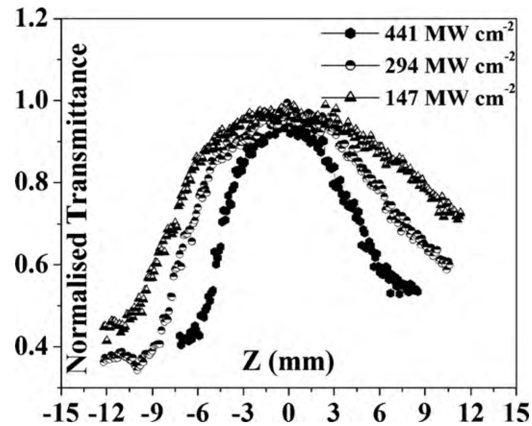

Fig. 3. Open aperture *z*-scan plot of rf PANI thin films in its pristine form for different laser fluences.

control over the film thickness was achieved by carefully controlling the time of deposition, monomer flow rate, vapour pressure and current density. A current density for the 8 A/m^2 was used in the present study for the preparation of polymer thin films.

The thickness of the thin films were measured using a *Dektak 6M* Stylus profilometer. In order to seek an insight into the mechanism of optical absorption, these films were subjected to UV–vis spectroscopy using a *Jasco 570* UV–vis–NIR spectrophotometer.

The open *z*-scan measurements were carried out by a Pulsed Nd:YAG laser, Quanta ray GCR 170, at a wavelength of 532 nm, with pulse energy (maximum) of 450 mJ. The pulse width is 6–7 ns and the pulse repetition frequency is 10 Hz, the spectral mode is Gaussian. The schematic of the experimental setup is given in Fig. 2. A detailed description of the experimental technique can be found elsewhere [3].

3. Results and discussion

3.1. Open aperture z-scan measurements on PANI thin films

The open aperture *z*-scan plot of rf PANI is shown in Fig. 3. It shows that the value of transmittance decay from the maximum absorbance value when the film moves away from the focus. It can be noticed that, as the input energy of the pumping beam increases,

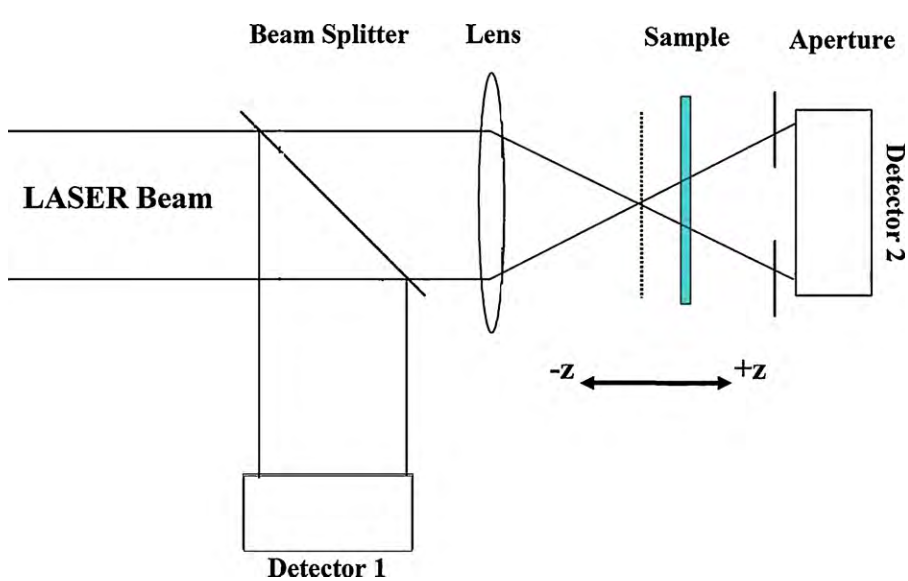

Fig. 2. Open aperture *z*-scan setup.