Final Technical Report

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"Poling of microwave electro-optic devices"

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The desire to transmit high frequency, microwave RF signals over fiber optic cables has necessitated the need for electro-optic modulation devices. Polymer electro-optic modulators offer a potential solution that may significantly outperform other electro-optic modulators, due to their inherently superior materials characteristics. Modulation frequencies in excess of 40 GHz are realizable using polymer electro-optic materials, as well as the additional potential benefits of low manufacturability and materials costs.

However, in order to reap these potential benefits, it is necessary to develop the devices and their associated fabrication processes, particularly those processes associated with the poling of the devices. To this end, we entered into a cooperative research agreement with Richard Kunath of NASA LeRC.

A graduate student in my group, Tony Kowalczyk, worked closely with the group at NASA to develop processes for construction of a microwave frequency electro-optic modulator. Materials were commercially obtained from Amoco Chemical and in collaboration with Lockheed-Martin. The photolithography processes were developed at NASA LeRC and the electric-field poling process was carried out in our laboratory at CWRU.

During the grant period, the poling process conditions were investigated for these multilayer devices. Samples were poled and the resulting nonlinear optical properties were evaluated in our laboratory. Following the grant period, Kowalczyk went to NASA under a NRC fellowship, and I continued to collaborate as a consultant. Publications listed at the end of this report came out of this work. Another manuscript is in preparation and will be submitted shortly.

Nonlinear optical materials must be formed into channel, slab, or rib waveguides for integrated optical applications. The resistance of crosslinked Amoco Chemical's Ultradel 9020D to organic solvents makes it a suitable material for layered devices. Three-layer slab waveguides by spinning and curing successive layers of Ultradel 9020D on ITO-coated glass. The layered structures were doped with one of two different nonlinear optical chromophores, DCM, which is commercially available and DADC from Lockheed-Martin. The molecule doped Ultradel 9020D cores were surrounded by neat Ultradel 9020D cladding layers. To obtain noncentrosymmetric ordering as well as large poling field induced nonlinearities in three-layered devices, it is essential for the cladding layers to be more conductive than the core layer so that the voltage drop, and hence the

poling field, across the active layer is as large as possible. Direct measurements of the poling field are not possible in three-layer samples because the voltage splitting between core and cladding layers is unknown. The effective poling field can be determined indirectly by measuring the macroscopic susceptibility's dependence on the externally applied field and comparing to theory. The macroscopic susceptibility was measured using the Rotational Maker Fringe (RMF) technique as a function of poling field for single- and three-layer samples.

Gold electrodes were sputtered onto the samples for contact poling. After contact poling, the gold was removed and the RMF experiment was performed. Measurements were made using the 2nd Stokes line $\lambda= 1.367$ μm of a hydrogen-filled Raman cell that was pumped by the output of a Nd:YAG pumped pulsed dye laser. The measured second harmonic coefficients in the single layer films for both dopants was found to agree with an oriented gas model. The agreement between theory and experiment shows that the oriented gas model adequately describes the poling induced ordering in polyimide materials.

The data for three-layer samples appear in Fig.1 for DCM- and DADC-doped samples. The two sets of data points on the graphs represent different methods of calculating the poling field across the active layer. The open data points assume the resistivities of all three layers are identical and the resulting poling field is obtained by dividing the applied voltage by the total thickness. The shaded data points use a scaling factor to fit the experimental data to the theoretical prediction with the poling field as an adjustable parameter. If we assume the three-layer sample can be modeled by resistors in series, then the scaling factor can be related to the cladding and core resistances by the following equation,

$$V_{eff} = \frac{R_{core}}{R_{core} + 2R_{cladding}} V_{applied} = UV_{applied}$$

where R_{core} and $R_{cladding}$ are the resistances of the core and cladding layers, and V_{eff} and $V_{applied}$ are the effective and applied poling voltages. The open data points show the inadequacy of assuming equal resistivities to determine the poling field across the active layer. For DCM triple-layers, a value of U=0.4 is used for the best-fit adjustable parameter, while for DADC triple-layers, a value of 0.11 is obtained. Conductivity of thin single-layer films was used to independently calculate the effective poling field. The conductivity and thickness of DADC triple-layers poled at 250 C predicts a correction factor of 0.1 in excellent agreement with the best fit. Thus, the voltage division model appears valid. For DCM triple-layers poled at 225 C theory predicts an effective poling field an order of magnitude smaller than the best fit adjustable parameter. This discrepancy may be due to migration of DCM into the cladding layers which lowers the conductivity of the core layer while increasing the conductivity of the cladding layers. This migration is consistent with the sublimation observed in single-layer films. The optimization of poling requires that the conductivity of the cladding be much larger than the core to maximize the electric field in the active layer.
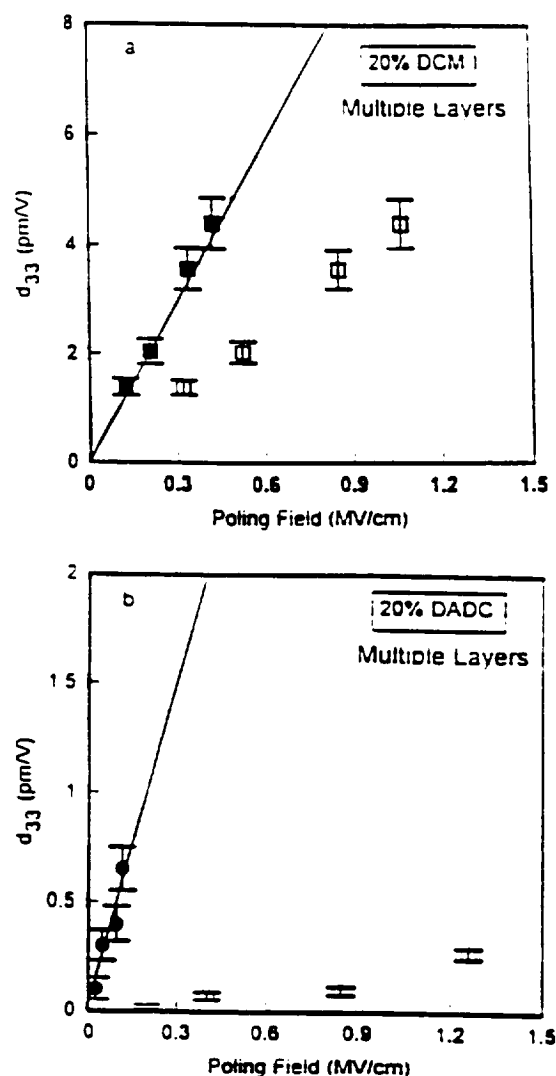
Figure 1. The nonlinear optical susceptibility versus poling field for three layer stacks of (a) DCM/Ultradel 9020D and (b) DADC/Ultradel 9020D. Solid lines represents fit to an oriented gas model. Data points are measurements from three-layer samples using the poling field as an adjustable parameter. Best results (shaded data points) are obtained using 0.4 as the best-fit parameter for DCM samples and 0.1 for DADC samples. (unshaded data points) assume that resistances of all layers are equal.

To this end, we have incorporated an ionic dopant consisting of a graft polymer incorporating a quaternary ammonium salt (used as an anti-static agent) into the cladding layers to increase the conductivity. A polymeric salt distributes throughout the cladding layers in contrast to small molecule salt that would reside at the surface. Measurements of the imaginary part of the dielectric constant that is proportional to the conductivity are

shown in Fig. 2 as a function of concentration. It is seen at low concentrations that the conductivity is nearly linear, but becomes exponential at higher concentrations. When the axis is scaled to the measured conductivities of the undoped polyimide and the DADC doped polyimides, the conductivity of the core layer is shown as a dotted line. We expect that the ionic doped layer at 18% loading will have the requisite conductivity to amplify the field in the core substantially. Fig. 3 depicts the second harmonic coefficient for a three layer film consisting of 18% ionic doped cladding and a core containing 15% DADC by weight. The line is a fit to the oriented gas model. The fit factor is about 0.3 indicating that the field is divided nearly equally between the three layers. This factor is considerably less than the value of 0.5-0.6 we would expect from the conductivity in Fig. 2 though substantially higher than the 0.11 without the ionic dopant. This discrepancy may be due to the decomposition or sublimation of the ionic dopant during the poling process. Refractive index measurements of the doped polymer before and after high temperature processing support this conclusion.
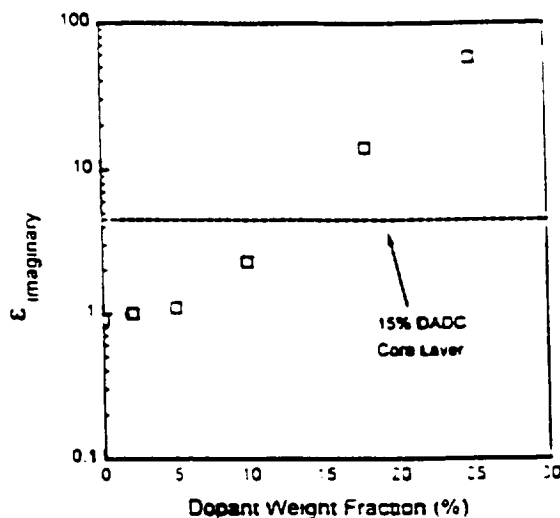

Figure 2. Imaginary dielectric constant for ionic doped polyimide. The dotted line indicates the approximate core equivalent conductivity.

Thus, we have successfully developed a poling process for multilayer electro-optic devices using ionic dopants in the cladding, which increases the effective electro-optic coefficient by several-fold. This improvement translates into better device performance by lowering the operating voltage of the device, thus reducing power consumption.
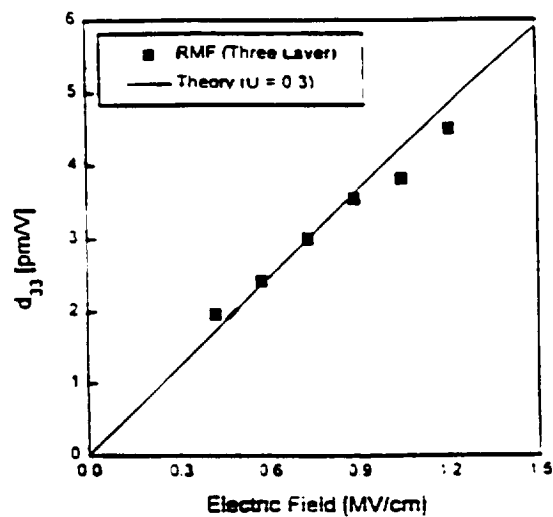
Figure 3. Three layer second harmonic coefficient data for three layer films with 18% by weight ionic doping in the core and 15% DADC doping in the core. Fit is to an oriented gas model.

1. K.D. Singer, T.C. Kowalczyk, H. Nguyen, A. Beuhler, and D. Wargowski, "Cross-Linked Polyimides for Integrated Optics", *Proc. SPIE* **CR68** (1997).

2. K.D. Singer, T.C. Kowalczyk, H. Nguyen, A. Beuhler, and D. Wargowski, "Cross-Linked Polyimides for Integrated Optics", *Proc. SPIE* **3006**, 326 (1997).