Keynote Paper

Biopolymers in Optoelectronics

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ABSTRACT

Here we demonstrate a 40% increase in the nonlinearity, or electro-optic (EO) coefficient, of the nonlinear optic (NLO) polymer SEO100 with the addition of a thin guanine nucleobase buffer layer deposited between the NLO polymer and the cathode electrode. We suggest that the high lowest unoccupied molecular orbital of guanine flattens the field distribution at the high injection barrier reducing leakage current during poling. This has the potential to realize higher EO coefficients without the need to synthesize new NLO polymer materials, as well as an increase in device yield due to less failure during poling.

Keywords: nonlinear optic polymer, opto-electronic, electro-optic modulator, electro-optic coefficient, guanine, nucleobase

1. INTRODUCTION

The nonlinear optical (NLO) polymer SEO100 has demonstrated an electro-optic (EO) coefficient, (r_{33}) as high as 160 pm/V.[1, 2] There are new variations of this material, such as SEO250, for which an r_{33} of 250 pm/V has been reported.[2] This has led to low device operational voltages.[1, 3] However, these operating voltages are still higher than expected, given these very high r_{33} materials.

For EO modulators, a 180° or π phase retardation is needed for the device to go from an on-state to an off-state. The voltage necessary to realize this π phase retardation ($V\pi$) is defined as the half wave voltage[4]

$$V\pi = \frac{\lambda d}{n^3 r_{33} L}, \tag{1}$$

where λ is the wavelength, d is the thickness of the EO material, n is the index of the EO material, r_{33} is the electro-optic coefficient of the EO material and L is the length of the interaction region. For a given geometry, the modulation voltage $V\pi$ will be inversely proportional to the EO coefficient r_{33}. Therefore, in order to minimize $V\pi$ one must maximize r_{33}.

However, equation (1) explains the behavior of a single layer device where the NLO material is sandwiched between two electrodes. For NLO polymer EO modulators a top and bottom cladding layer must be added between the NLO polymer and the electrodes. This configuration allows for better confinement of the optical beam in the core and reduces the optical loss. To take the additional cladding layers into account, equation (1) becomes[5]

$$V\pi_{\mathrm{Operation}} = \frac{\lambda}{n^3 r_{33} L} \cdot \left(d_{\mathrm{Core}} + d_{\mathrm{CladB}} \cdot \sqrt{\frac{\varepsilon_{r\mathrm{Core}}}{\varepsilon_{r\mathrm{CladB}}}} + d_{\mathrm{CladT}} \cdot \sqrt{\frac{\varepsilon_{r\mathrm{Core}}}{\varepsilon_{r\mathrm{CladT}}}} \right), \tag{2}$$

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where $V\pi_{operation}$ is the voltage necessary to realize a π phase retardation at the modulation frequency in the three-layer EO modulator device, d_{Core}, d_{CladB} and d_{CladT} are the thicknesses of the NLO polymer, bottom cladding material and top cladding material, respectively, and ε_{rCore} ε_{rCladB} and ε_{rCladT} are the dielectric constants of the NLO polymer, bottom cladding material and top cladding material, respectively, at the modulation frequency.

With cladding layers as thick as the core layer or, in typical cases, as much as twice as thick as the core layer to ensure the lowest optical loss, the best performance that can be realized is $V\pi_{operation} = V\pi/5$ to $V\pi_{operation} = V\pi/3$, where $V\pi$ is the half wave voltage for the single layer device. Therefore, it becomes most important for r_{33} to be as high as possible. This is why development of new NLO polymer materials has been on-going, synthesizing new materials with higher and higher r_{33s}.

For NLO polymers, the value for r_{33} is determined by applying a high electric field, or poling field, across the active polymer film after heating to near its glass transition temperature T_g and then allowing it to cool to room temperature, while keeping the electric field applied. Also, the magnitude of the EO coefficient for any guest/host NLO poled polymer is proportional to the applied poling field. Thus, it is desired to maximize the poling field to just less than that which would result in dielectric breakdown of the material. See Fig 1.[6]

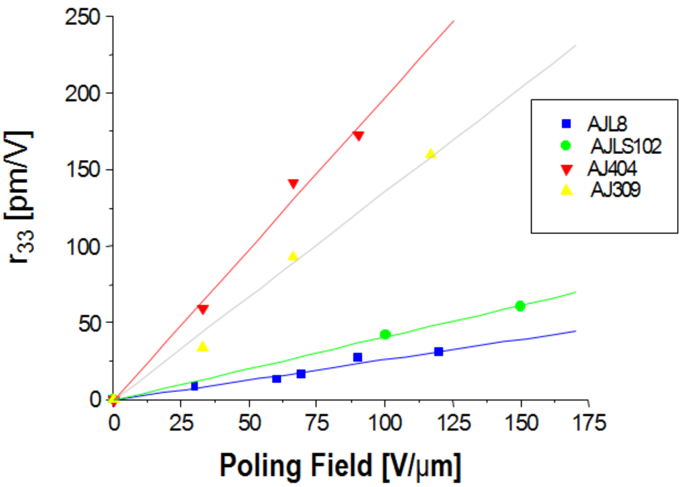

Figure 1. r_{33} versus poling field for several NLO polymers[6]

The typical poling field for NLO polymers is around 100 V/µm. There have been cases where these materials have been poled at higher fields, see Fig 1., however most of the devices end up breaking down under the higher fields, reducing the yield. So, in order to keep device yields up, the poling field is kept to around 100 V/µm.

When fabricating NLO polymer EO devices, one needs to account for any additional layers making up the device. These include the cladding layers as well as any buffer layers. To determine how much of the applied voltage is dropped across the NLO polymer core material, the thicknesses and relative electrical resistivities of all the materials between the electrodes need to be taken into consideration. One can treat the stack as a standard DC ohmic voltage divider.[5]

In order to maximize the value of r_{33}, for the waveguide structure, the relative electrical resistivity of the claddings and any buffer layers must be lower than that of the NLO polymer core material. In practice, we have found that the electrical resistivities of the claddings and any buffer layers must be at least 10X lower than that of the NLO polymer core.

However, even meeting this requirement, we are still limited to 100 V/µm poling fields in order to prevent electric field breakdown and maintain device yield high.

Jen's group, at the University of Washington, introduced a thin sol-gel derived titanium dioxide (TiO_2) layer between the anode electrode and NLO polymers AJ307, AJ-CKL1, AJ404[2] and SEO100 to increase r_{33}.

They demonstrated a 26% to 40% increase in r_{33}, compared to structures without the TiO_2 layer, achieving an r_{33} as high as 226 pm/V.[2] The sol-gel derived TiO_2 was spin deposited on top of an indium tin oxide (ITO) electrode coated substrate and then annealed at high temperature (~400C) under O_2 to crystallize the obtained films. Titanium oxide films have a very low electrical resistivity compared to the NLO core and was practically conductive (1.5×10^{-4} S/cm).

They claimed that it behaved like a transparent electrode that blocked excessive charge injection, thus reducing the leakage current during poling. The r_{33} enhancement was believed to be due to a field distribution flattening effect at the high injection barrier. They proposed that the low valence band blocked hole injection form the anode.

2. EXPERIMENTAL

We fabricated similar devices to those of Jen's group using SEO100, provided by Soluxra, and achieved similar results, using Teng Man,[7] for not only the polarity of the poling voltage they presented in their paper[2], but for reversed polarity of the poling voltage, as well.

This suggested to us that maybe the enhancement in r_{33}, using the TiO_2 layer, has more to do with smoothing out the surface of the ITO, which is very rough, 25 nm for ITO 100 nm thick,[8] than it has to do with blocking hole injection. Smoothing the ITO surface would, in-turn, render the applied electric field much more uniform across the NLO polymer and realize a much higher poling efficiency.

If a TiO_2 layer on the anode side could increase r_{33}, could a material with a high conduction band, or one with a lowest unoccupied molecular orbital (LUMO), on the cathode side of the device work as well?

For comparison with Jen's group, we used SEO100 for the NLO polymer. For the cathode side material, we used the nucleobase guanine. It has a LUMO level closer to vacuum than SEO100 and has a lower electrical resistivity than SEO100. Not as low as TiO_2, but low enough to prove the concept. A 60 nm guanine layer was vapor deposited on top of a 1 µm thick layer of SEO100, which had been spin deposited on an ITO coated substrate. A gold electrode was deposited on top of the guanine. A poling field of 100 V/µm was applied to both the devices with the guanine layer and without the guanine layer (control devices).

3. RESULTS

The r_{33} we achieved for the control devices (without the guanine layer) measured ~89 pm/V. Much lower than Jen's group, however the SEO100 we used was more than 1 year old and we were looking for relative changes compared to the control devices and not for achieving the highest r_{33} to date.

The r_{33} achieved for the devices with the guanine layer measured ~127 pm/V. This is a 40% increase, compared to the control devices, and is very similar to Jen's group's results using TiO_2. We then reversed the poling polarity and achieved similar results. The same thing we observed using TiO_2. This suggests that, like with TiO_2, addition of the guanine layer has more to do with smoothing out the surface of the electrode, than it has to do with blocking any charge carrier injection.

4. SUMMARY

In summary, we have demonstrated increased r_{33} using a guanine nucleobase buffer layer between the cathode electrode and the NLO polymer SEO100. One could hypothesize that even though the TiO2 and guanine are most likely blocking charge carrier injection, their main contribution to the increase in r_{33} has more to do with smoothing the interface between the electrodes and the NLO polymer. More work is needed. But, whatever the specific reasons, introduction of both the TiO2 and guanine demonstrate a significant improvement in r_{33}. Our next phase of research will include fabricating and testing devices which include both TiO2 on the anode side and guanine on the cathode side.

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