CHAPTER 5

Conclusions

In this dissertation, optical and electro-optic properties of II-VI semiconductor nano-clusters and electro-optic polymers are investigated, electro-optic films are fabricated by ESA process, and the unique structure and properties of ESA films are explored.

II-VI semiconductor nano-clusters have been synthesized, with particle diameters ranging from 4 nm to tens of nanometers, which are comparable with the Bohr radii of CdSe and CdS crystals. The diameter can be controlled by controlling reaction time and temperature. In order to make high quality nano-clusters, the synthesis temperature should be higher then 300C. There is a difference in peak positions of absorption and photo luminescence spectra, related to defect states in nano-crystals. Particle sizes measured by absorption spectrum and by HRTEM are very close. Based on quantum mechanical theory, wavelength shifts as a function of particle size (blue shift) can be predicted, but the theoretical results are far from the experimental results, since in practice, more factors other than particle size affect the shift.

By dispersing nano-clusters in a polymer host, two kinds of electro-optical films are fabricated. One is by the ESA process, another is by the spin coating process. ESA films have much stronger absorption than spin coated films, and a slight blue shift in peak

position wavelength. Photo luminescence spectra also show a blue shift of ESA films with respect to spun films. One reason for this is an internal field induced shift, due to the different structure of these two films. Another reason is a particle size induced shift. Control of the pH value of the cationic solution is important, in that higher pH results in thicker film per bilayer, but resulting film growth is not uniform, absorption and film thickness do not increase linearly with the number of bilayer (or dipping times). At low pH, the film grows uniformly, but the thickness per bilayer is low.

Polymeric electro-optic films may be fabricated by the ESA technique. Effects of applying an external electrical field during the ESA process on film growth and properties have also been investigated. Peak position, optical density and wavelength at maximum absorption, all increase with number of bilayers, and films made under external fields have lower absorption and peak wavelength than those of films fabricated without an external field. These results are related to the order parameter, and indicate that molecule alignment can be improved by the application of an external field during the process of ESA film growth, and these results can be used to explain the unusually electro-optic properties of nano-cluster and polymer films fabricated by ESA.

CdSe nano-clusters have a much higher electro-optic coefficient than their bulk crystal counterparts. They have totally different origins in their electro-optic effects. For both nano-cluster-and chromophore based ESA films, their electro-optic coefficients are higher than those of spin-coated films, and no poling voltage is needed. The r_{33} of spin coated films vary with nano-cluster concentration, and there is a critical concentration at which the maximum electro-optic coefficient can be obtained.

Electro-optic coefficient decreases with frequency, and CdSe quantum dots need 17. 5 ms to complete their physical orientation due to a rotation of its permanent dipole moment. Therefore, at lower frequencies (<100Hz), electro-optic modulation mainly stems from the orientation of the permanent dipole moment. At frequencies higher than 100 Hz, the electro-optic modulation mainly arises from the induced dipole moment orientation and pure electron movement.

The ratio of the electro-optic coefficients $r_{333}/r_{113} > 3$. This means that ESA films cannot be treated as an ideal isotropic system with the C∞v symmetry, and interactions should be considered. Quadratic Kerr electro-optic coefficients have a similar frequency dependence to that of the linear electro-optic coefficients r_{333} and r_{113}. This indicates that the orientational distribution of the CdSe quantum dots particularly contributes to the quadratic electro-optic modulation.

The stability of electro-optic polymer films is studied, Proton irradiation can break the N=N double bonding in π-conjugated bridges, leading to damage of the conjugating structure, so causing a decrease of the EO coefficient. Thermal and temporal stability of ESA films are much better than that of spin coated films; this is a significant feature of ESA technique.

Based on the properties of electro-optic films, the applications of polymer and nano-cluster electro-optic films are discussed. The focus has been on the basic configurations and dimensions of MZI electro-optic intensity modulators. Nano-cluster CdSe electro-optic film has a higher refractive index than the PS-119 polymer film, which are close to that of silica glasses, so silica glasses are the ideal substrates for those films, while semiconductor wafers are not useful. By analysis, the cutoff thickness was

determined, for single mode (m=0); they are approximately 400 nm for CdSe film and 2500 nm for PS-119 film.

The effective refractive index as a function of the sizes of waveguide are calculated. The aspect ratio w/t, w, and t are determined versus the refractive index of the electro-optic films. We have consider w/t=4.1 for PS-119 film, and w/t=1.1 for CdSe film. For high speed operation, traveling wave electrode designs were considered, based on effective refractive index and impedance matching. The effective dielectric constant and characteristic impedance as a function of electrode structure were diagramed, and this served as a basic design suggestion for traveling wave electrodes. Compared to electro-optic inorganic crystals, electro-optic polymer and nano-cluster based composite films are easer to achieve better device performance.

VITA

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Fajian Zhang was born and raised in China. He completed his undergraduate studies in Materials Engineering in 1985 from Northwest University of Light Industry, and he completed his graduate studies in Materials Science and Engineering in 1991 from Tianjin University, then he was working as a faculty member in the Department of Materials Science and Engineering in Southwest Jiaotong University in China. He joined the Department of Materials Science and Engineering at Virginia Polytechnic Institute and State University, under the supervision of Dr. R. O. Claus. His graduate studies and researches were focused on solid state materials and devices and fiber optics. Here He won Master of Engineering (MEng) degree in 2001 and Doctor of Philosophy (Ph. D.) degree in 2002. After completing his graduate studies in 2001, he was working as an engineer in Cirrex Corp. to develop integrated opto-electronic systems (OCHIPs) in his Optional Practical Training (OPT) period. Since 2002, he has been with Fiber and Electro-optic Research Center in the Bradley Department of Electrical and Computer Engineering at Virginia Polytechnic Institute and State University as a research staff.