

Acknowledgements

This dissertation could not have been finished without the help and support from many professors, research staff, graduate students, colleagues and my family. It is my great pleasure to acknowledge people who have given me guidance, help and encouragement.

I would like to first thank Dr. R. O. Claus for his constant guidance, personal attention, suggestions and endless encouragement and full support during last four years of my graduate study and research. He gave me opportunities to participate in this research program, and to work with talented research staff and graduate students in his research center.

Special thanks go to my advisory committee members professor William B. Spillman, Jr., professor Diana Farkas, professor Guo -Quan Lu, and professor Louis Guido for their endless, important suggestions and remarks in this research program and for their time and effort in service on my doctoral committee despite their already heavy loads of responsibility.

I would like to express my sincere appreciation to research scientists Dr. Liangmin Zhang, Dr. Youxiong Wang, and Dr. Tingying Zeng, who gave me enormous valuable discussions, technical support and hands -on help in many aspects of this research program, and their caring and concern about this dissertation.

My special appreciation goes also to Professors Jin Z. Zhang and Dr. Michael C. Brelle in the Chemistry and Biochemistry Department, University of California Santa Cruz, who provided generous femtosecond ultrafast lasers spectroscopy measurements. They also gave me much information and discussion in this respect. Thanks also go to professor Sandra J. Rosenthal in the Chemistry Department of Vanderbilt University for her assistance with the preparation of CdSe nanocrystals.

It has been my pleasure to work with graduate students and colleagues in the Fiber & Electro-Optics Research Center, they are Roger Duncan, Cathy Hui, and Qiao Chen. We discussed together, exchange ideas, and helped each other. Those made my years at Virginia Tech the most memorable period in my life.

Finally, I would express my gratitude to my parents, my parents-in-law, my wife and my son and my brothers, whose support and constant encouragement helped me through the hard times of this program. My deepest appreciation is expressed to them for their love, understanding, and inspiration. Without their blessings and encouragement, I would not have been able to finish this work.

Table of contents

Chapter 1. Introduction	1
1.1 Electro -optic and nonlinear optical properties of materials	2
1.2 Electro -optic devices	6
1.3 Objectives of research	9
1.4 References	12
Chapter 2. Preparation and Optical Properties of III -V Semiconductor Nano -cluster and Polymeric Electro -optic Films	15
2.1 Introduction	15
2.1.1 General theories and concepts concerning semiconductor nano -crystals	15
2.1.2 Preparing of Semiconductor nano -clusters	22
2.2 Films preparing	25
2.2.1 Electrostatic self -assembly (ESA) technique	25
2.2.2 Spin coating of nano -particledoped polymeric EO films	28
2.2.3 Poling of spinning coated electro -optic films	29
2.3 Characterization of fabricated nano -clusters and EO films	31
2.4 Experimental procedure	32
2.4.1 III -V semiconductor nano -crystals and films preparation	32
2.4.2 Preparing of electro -optic films by ESA technique	33
2.4.3 Spin coating of nano -particledoped polymeric EO films	34

2.5 Results and discussion	35
2.5.1 Absorption and PL spectra and nano -cluster synthesis	35
2.5.2 Analysis of the shift of absorption spectra because of particle size	44
2.5.3 Internal field of films induced by ESA process	47
2.5.4 Comparison and process controlling of film growth by ESA technique	54
2.5.5 Stability of nano -cluster and polymeric electro -optic films	60
2.6 Conclusions	65
2.7 References	67
Chapter 3. Electro -optic Properties of II -VI Semiconductor Nano -clusters and Electro - optic Chromophores	69
3.1 Introduction	69
3.1.1 Electro -optic properties of semiconductor nano -cluster materials	69
3.1.2 Electro -optic properties of electro -optic chromophores	76
3.2 Measurements of Electro -optic Pockels and Kerr coefficients	81
3.2.1 Linear electro -optic coefficient measurement by ellipsometric setup	83
3.2.2 Linear Electro -optic coefficient measurement by MZI setup	88
3.2.3 Quadratic electro -optic coefficient measurement by ellipsometric setup	91
3.3 Results and discussion	95
3.3.1 Polymer matrix nano -cluster electro -optic films	95
3.3.2 Polymeric electro -optic chromophore films	116
3.4 Conclusions	130
3.5 References	131

Chapter 4. Application of Electro-optic Materials: Design of Polymeric Optical Modulators	135
4.1 Introduction	135
4.2 Waveguide analysis by means of effective index approach	139
4.2.1 Minimum (cutoff) thickness of planar waveguide	139
4.2.2 Channel (ridge) waveguide	144
4.3 High speed operation and traveling wave electrode design	148
4.3.1 High speed device	148
4.3.2 Traveling wave electrode design	154
4.4 Waveguide and electrode fabrication	158
4.5 Conclusions	159
4.6 References	160
Chapter 5. Conclusions	162

List of Figures and Tables

Fig.1 -1. Structure of MZI modulators: Basic cosine response of a MZI modulator.	7
Fig.1 -2. Power-length product as a function of switching speed of some electro-optic and nonlinear optical materials.	9
Fig.2 -1. Densities of states for 3D, 2D, 1D, and 0D systems.	18
Fig.2 -2. Enhanced confinement and oscillation strength in compressed excitons.	20
Table 2.1. Number of total atoms and percentage of surface atoms vary with radius of nano-clusters.	21
Fig.2 -3. Formation of surface capped semiconductor nano-crystals.	23
Fig.2 -4. ESA schematic for build up of multilayer assemblies by consecutive absorption of anionic and cationic molecule-based polyelectrolytes.	27
Fig.2 -5. ESA processing of polymers in combination with water-soluble nano-cluster quantum dots allows wide variation of thin-film properties.	27
Fig.2 -6. Needle coronapoling setup. (a) Configuration; (b) Picture of poling setup.	30
Fig.2 -7. Room temperature absorption spectra of CdS, CdSe and CdTe nano-crystallites with different particle sizes. (a): 2-3 nm diameter of CdSe, CdS, and CdTe nano-particles, (b): CdSe nano-particles at various sizes.	32
Fig.2 -8. Pictures of various films ready for measurements.	35
Fig.2 -9. Optical absorption spectrum of CdS nano-particles dispersed in pyridine.	37

Fig.2 -10.LuminescencespectrumofCdSsolution(CdSdispersedinpridine).	
Peak intensityisat526.6nm.	37
Fig.2 -11.OpticalabsorptionspectraofCdSefilmsandsolution.	40
Fig.2 -12.LuminescencespectraofCdSefilmsfabricatedbyspincoating andESA.	40
Fig2 -13.TEM(A)anddiffractionring(B)ofCdSnano-clusters.	3
Fig.2 -14.TEM(A)anddiffractionring(B)ofCdSenano-clusters.	43
Fig.2 -15. Calculatedabsorptionbandedgevarieswiththediameter ofCdSquantum dots.	46
Fig.2 -16. Calculatedthresholdwavelengthshiftvarieswiththediameter ofCdS quantumdots.	46
Fig. 2-17.Maximumabsorptionvarieswiththickness(numberoflayers) andexternal voltageofPS -119/PDDAfilmswithandwithout external electricalfield.	49
Fig.2 -18.Opticaldensityvarieswiththickness(numberoflayers)and externalvoltage ofPS -119/PDDAfilmswithandwithout externalelectricalfield.	49
Fig.2 -19.Peakwavelengthvarieswiththickness(numberoflayers)and external voltageofPS -119/PDDAfilmswithandwithoutexternal electricalfield.	50
Fig.2 -20.OpticalabsorptionspectraofPS -119/PAHfilmswithdifferent thickness (numberofbilayers).	55
Fig.2 -21.AbsorptionvarieswithnumberofbilayersofPS -119/PAHfilms	

- at peak position. 55
- Fig. 2 -22. Optical absorption spectra of PS -119/PDDA films with different thickness (number of bilayers). 56
- Fig. 2 -23. Absorption varies with number of bilayers of PS -119/PDDA films at peak position. 56
- Fig. 2 -24. AFM diagram of PS -119/PAH film, 200 bilayers. 57
- Fig. 2 -25. AFM diagram of PS -119/PDDA film, 75 bilayers. 57
- Fig. 2 -26. Absorption spectrum versus number of bilayers, pH value of PDDA solution is 5.8. 58
- Fig. 2 -27. Absorption spectrum versus number of bilayers, pH value of PDDA solution is 11.5. 58
- Fig. 2 -28. Absorption varies with number of bilayers of CdSe/PDDA films at peak position (585 nm), pH value of PDDA solution is 5.8 and 11.5. 59
- Fig. 2 -29. XPS spectrum of CdSe -PDDA film made by ESA process, pH value of PDDA solution is 11.5, concentrations are: Cd=6.20, Se=2.08 (atomic %). 63
- Fig. 2 -30. XPS spectrum of CdSe -PDDA film made by ESA process, pH value of PDDA solution is 11.5, concentrations are compound Se=43.42, alloy Se=56.58 (atomic %). 64
- Fig. 2 -31. XPS spectrum of CdSe -PDDA film made by ESA process, pH value of PDDA solution is 5.8, concentration is Cd=6.14, Se=3.48 (atomic %). 64
- Fig. 3 -1. Relevant energy levels for SDGs (semiconductor nano -crystals dispersion in glasses) in the resonant regime. 73

Fig.3 -2.Schematicenergylevelschemediagramforthebulksemiconductor andfor themicro -crystallite.	74
Fig.3 -3.PlotsofIm $\chi^{(3)}$ andRe $\chi^{(3)}$ as a function of frequency, ω_0 is the resonance frequency.	75
Fig.3 -4.3kinds ofelectro -opticpolymers.	79
Fig.3 -5. Ellipsometricsetup.	84
Fig.3 -6.Pictureofellipsom etricsetup.	85
Fig.3 -7.Mach -Zehnderinterferometricsetupforlinearelectro -opticeffect measurements.	94
Fig.3 -8.PictureofMach -Zehnderinterferometricsetup.	95
Fig.3 -9.Modulationfrequencydependentofr r_{33}/r_{113} ratioofnano -cluster CdSe/PDDA ESAfilm.	96
Fig.3 -10.r r_{33} varies with modulation frequency of CdSe films fabricated at different conditions, poling voltage is 80 volts/micron.	98
Fig.3 -11.r r_{33} varies with poling voltage of spin coated CdSe films.	104
Fig.3 -12. r_{33} of CdSe/Nor -65 film versus CdSe concentration, poling voltage 80 volts/micron, modulation frequency 300 Hz.	106
Fig.3 -13.r r_{33} as a function of modulating frequency measured using the Mach-Zehnder setup.	110
Fig.3 -14.r r_{113} as a function of modulating frequency measured using the Mach-Zehnder setup.	110
Fig.3 -15.r r_{113} as a function of modulating frequency measured with the ellipsometric setup.	115

Fig.3 -16.r	333asa	functionofmodulatingfrequency measuredwiththe ellipsometric setup.	115
Fig.3 -17.		Molecularstructuresofvariouspolymersusedinthe present work.	118
Fig.3 -18.		Modulationfrequencydependenceofr ₁₁₃ ofESACL D/PDDAfilm.	119
Fig.3 -19.		Modulationfrequencydependenceofr ₃₃₃ ofESACL D/PDDAfilm.	120
Fig.3 -20.		Modulationfrequencydependenceofr ₃₃₃ andr ₁₁₃ ofspincoating CLD/PDDA(wt.31%CLD)film.	120
Fig.3 -21.r	333,r ₁₁₃	varywithfrequencyofmodulationvoltageof PS-119/PDDA films.	123
Fig.3 -22.r	333,r ₁₁₃	varywithfrequencyofmodulationvoltageofproton irradiatedPS -119/PDDAfilms.	123
Fig.3 -23r	333,r ₁₁₃	varywithfrequencyofmodulationvoltageof PCBS/PDDAfilms.	124
Fig.3 -24.r	333,r ₁₁₃	varywithfrequency ofmodulationvoltageofproton irradiated PCBS119/PDDAfilms.	124
Fig.3 -25.	FT -IR	ofpolys -119/PDDAESAfilmswith(1 -A)andwithout (control-A) protonirradiation.	125
Fig.3 -26.	FT -IR	ofPCBS/PDDAESAfilmswith(3A)andwithout (control3)proton irradiation.	125
Fig.3 -27.r	333	ofPS -119/PDDAatdifferentthickness(240,378and540bilayers).	126
Fig.3 -28.r	33,r ₁₃	varywithpolingvoltageofPS -119/PDDAfilm(540bilayers), modulationfrequency1000Hz.	127
Fig.3 -29.r	33	varywithmodulatedfrequencyofBR/PDDAfilm.	127

- Fig.3 -30. Electro-optic coefficient of ESABR/PDDA films at different thickness. 128
- Fig.3 -31. Electro-optic coefficient of PS-119/PDDAES films vary with number of bilayers with and without applied field in the process of film growth, modulation frequency is 30Hz. 129
- Fig.4 -1. Schematic of channel waveguide structure (left hand) and top view of waveguide multilayer (right side). 136
- Fig.4 -2. Configuration of planar waveguide. 141
- Fig.4 -3. Dispersion curve of ESAPS-119 and CdSe films. 142
- Fig.4 -4. High frequency (optical) dielectric constant of ESAPS-119 and CdSe films. 142
- Fig.4 -5. Cutoff thickness of planar waveguide varies with refractive index of core layer, $n_1=1$, $n_3=1.50$, wavelength=1550nm. 142
- Fig.4 -6. Cutoff thickness of planar waveguide varies with refractive index of cladding layer, $n_2=1.51$ and 1.61 , $n_3=1.50$, wavelength=1550nm. 143
- Fig.4 -7. Configuration of 3-D channel waveguide. 145
- Fig.4 -8. Effective refractive index versus core layer thickness. 145
- Fig.4 -9. As a function of normalized frequency of 3-D channel waveguide. 146
- Fig.4 -10. Ultrafast laser spectroscopy of CdSe nano-cluster doped glass at different pulse intensity. 149
- Fig.4 -11. Modulation index as a function of modulation length at different modulation frequency, $n=1.51$, $n_m=1.56$. 152
- Fig.4 -12. Modulation index as a function of modulation length at different n_m , $n=1.51$, $\omega_m=100$ GHz. 152

Fig.4 -13.Illustrationoftravelingwave.	154
Fig.4 -14. Effectivedielectricconstantasfunctionofelectrodesizes	.157
Fig.4 -15. Characteristicimpedance asfunctionofelectrodesizes.	157