Development of Field-controlled Smart Optic Materials
(ScN, AlN) with Rare Earth Dopants

Hyun Jung Kim[1,a], Yeonjoon Park[1,b], Glen C. King[2,c], and Sang H. Choi[2,d]

[1]National Institute of Aerospace (NIA), 100 Exploration Way, Hampton, VA 23666 USA

[2]NASA Langley Research Center, MS 188A, Hampton, VA 23681-2199 USA

[a]Hyunjung.Kim@NASA.Gov, [b]Yeonjoon.Park-1@NASA.Gov, [c]Glen.C.King@NASA.Gov, [d]Sang.H.Choi@NASA.Gov

Abstract
Development of the fundamental materials for field-controlled spectrally active optics is essential for new concept of optics, such as: membrane optics, filters for LIDARs, windows for sensors and probes, telescopes, spectroscopes, cameras, light valves, light switches, flat-panel displays, etc. The dopants of rare earth elements create a number of absorption and emission band structures and can easily be incorporated into many high quality crystalline and amorphous hosts. In wide band-gap semiconductors, like ScN and AlN with rare earth dopants, the existing deep levels can capture or emit the mobile charges, and can be ionized with the loss or capture of the carriers. This is a fundamental basis for smart optic materials. ScN and AlN doped with rare earth elements (Er, Ho) were tested under an applied electric field to characterize spectral and refractive index shifts by the Stark Effect. Decrease in refractive index under an applied electric field was observed as a shift in absorption coefficient using a variable angle spectroscopic ellipsometer. Under an electric field, mobile carriers are redistributed within the space charge region (SCR) to reveal this electro-refractive effect. The main research goal is to facilitate concept demonstration and testing of field-controlled spectrally smart active optics for optical multi-functional capabilities in a selected spectral range.

Introduction

The electro-absorption (EA) effect is defined as the change of optical absorption in the presence of an electric field. This effect was first studied by Franz [1] and Keldysh [2] in bulk semiconductors and was called the Franz-Keldysh effect. The Franz-Keldysh EA effect can be described as the below-band-gap photon-assisted tunneling of electrons from the valence to the conduction band in the presence of the electric field. A full description of such an inter-band optical absorption should include the effects of the Coulomb interaction of the electron and hole [3,4].

The effects on atomic and molecular energy level and associated spectra by externally imposed electric fields become apparent with a separation of the degenerative levels into specific angular momentum states. This effect is known as the Stark effect [5]. As compared to the intrinsic Stark effect, due to the quantum transitions of bound or transitional electrons, the quantum-confined Stark effect (QCSE) is based on charge carriers that undergo redistribution within materials, according to the strength of the applied electric field. A quantum confined Stark effect (QCSE) optical modulator element has one or more quantum wells bounded by asymmetric barriers. This provides a device in which the direction and magnitude of the electric field-induced absorption edge shift corresponds to the applied electric field's polarity and intensity. In the semiconductors the dopant states and mid-bandgap states determine the space charge region. The finite number of carriers, electrons and holes, are mobilized according to the applied electric field. The redistribution of these charged carriers determines the absorption wavelength of light into the device layers. The light absorption variations can be described by the Kramers-Kronig relations (KKR) that explain the

changes in the real refractive index [6]. The index of refraction is determined by the change in the absorption coefficient in the media as shown by the KKR. Therefore, an external electric field can influence certain media, resulting in changes to its index of refraction. The change in refractive index is controlled by the density, energy state, and location of deep levels in this model. Additional deep level transition spectroscopy measurements can identify the embedded deep levels in ScN and AlN films. The semiconductor hosts, such as ScN and AlN doped with RE offers a photonic transition at UV range.
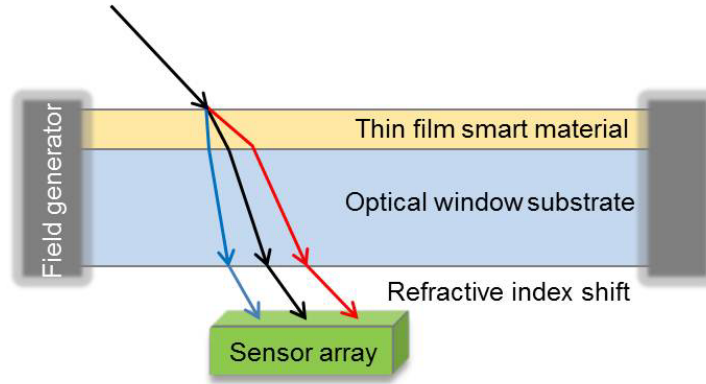

Figure 1. The concept of spectrally active smart optics with Stark effect

Figure 1 shows the concept of spectrally active smart optical window. The thin film with the Stark effect is grown on an optical window substrate for smart active spectral selection. This film offers a spectral selection capability by physically shifting the transmitting spectral components with the variable injection of electric field. The rare earth (RE) elements form a group of elements that have a partially filled $4f$ shell, and usually take on a 3+ ionic state (RE^{3+}) of which energy levels are predominantly independent of their surroundings. In general, the $4f$ electronic energy levels of RE ion are shielded from external fields by $5s^2$ and $5p^2$ outer-shell electrons. Many of the RE elements in lanthanide series with atomic numbers 58 through 70, are categorized as phosphor materials and therefore, considered as doping materials for the smart active optics applications.

Experimental method

DC-and RF-magnetron sputtering methods were used for the growths of ScN, Er-doped ScN, Ho-doped ScN, AlN, and Er-doped AlN on 2-inch quartz substrates. The substrates were degreased in acetone and isopropyl alcohol, rinsed in deionized water, and blown dry in N_2 gas before they were introduced into the chamber for baking under the infrared heat at 200°C for 1 hour. The films were grown at 850°C with the injection of 7 sccm flow of N_2-Ar mixture gas while keeping the chamber pressure at 7 mTorr. The DC power of 100 W and RF power of 5 W were applied to the Sc (or Al) and rare earth materials, respectively. The optical absorbance spectra of the films were measured for band gap calculation by UV/VIS/NIR Spectrometer (Lambda 900, Perkin Elmer). Advanced electrical characterization was performed for mobile carrier density and conductivity with Hall Effect measurement (HEM-2000, EGK). All films were then measured by Variable Angle Spectroscopic Ellipsometry (VASE, WVASE32, J. A. Woollam) over the range of 1.1-5.0 eV, and 57 to 77 degrees with a 2 degree interval. Optical measurements of samples were made under 0, 1000, and 1500 volts DC applied through the thickness of the specimen. The rear voltage probe was in contact with the quartz substrate, while the front contact was placed ~2 mm above the surface to facilitate the pass-through of incident and reflected light during the measurements. All data was fitted with a Lorentz model between 2 and 5 oscillators depending on the sample. Optical constants were recorded for the best-fit model. Data was taken at each of the two or three voltage values without moving the sample of voltage probe to eliminate the positioning effects. A point to point (PTP) fit to the optical constants of the AlN and AlN-doped Er were made.

Results and discussion

The UV-Vis spectrum of ScN, Er-doped ScN, and Ho-doped ScN thin films measured at room temperature were plotted as shown in Figure 2.
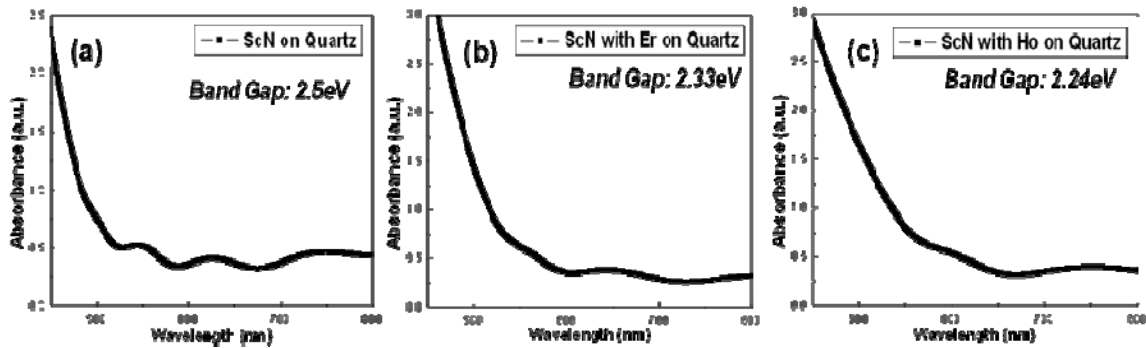

Figure 2. Absorbance (A) as a function of wavelength (λ) for optical band gap calculation of (a) ScN, (b) Er-doped ScN, and (c) Ho-doped ScN

Using the absorption spectra data, the optical band gaps (E_g) of ScN, Er-doped ScN, and Ho-doped ScN were calculated [7,8]. The estimated band gaps of Er-doped ScN and Ho-doped ScN were about 2.33 eV and 2.24 eV, respectively. The values of band gap of Er-doped ScN and Ho-doped ScN are smaller than that of thin film ScN (2.4 eV). When impurities were introduced into the ScN nanostructures/thin films, they can modulate the locality structure and cause the observable change of optical properties. Therefore, the spectral shifts through the absorption onset from the prepared Er-doped ScN and Ho-doped ScN thin films, as compared with that of the ScN thin film phase, may be caused by the Er and Ho dopants. In addition, the absorption peak of the UV-visible spectrum becomes much broader than a lower energy shift. This supports the reduced band gap energy levels (E_g) and the energy broadening of valence band states attributable to the dopant. As the doping element enters into the ScN crystal lattices, the localized band edge states form at the doped sites with a reduction of E_g.

The shifts in refractive index (n) and extinction coefficient (k) of the ScN and Er-doped ScN films, shown in Figure 3 (a) and (b) and, were developed on a quartz substrate with respect to the applied voltage. The decrease n with applied field is observed with smaller shift in k as shown in Figure 3. The spectral shifts are clearly observed from 4eV to higher photon energy. The index of refraction (n) and extinction coefficient (k) of the film were measured with 0, 1000V, and 1500 volts applied through the thickness. This is good example of a material showing Stark effects [9,10]. ScN thin film shows a spectral shift above 4eV and Extinction coefficient data shows a spectral shift above 4eV and intensity decrease through the entire photon energy (wavelength) range from 1eV to 5eV. ScN doped with Er (b-1, 2) shows intensity decrease through the entire photon energy range with no spectral shift. (This is discussion point and not in figure description; perhaps it was just formatting issue.)
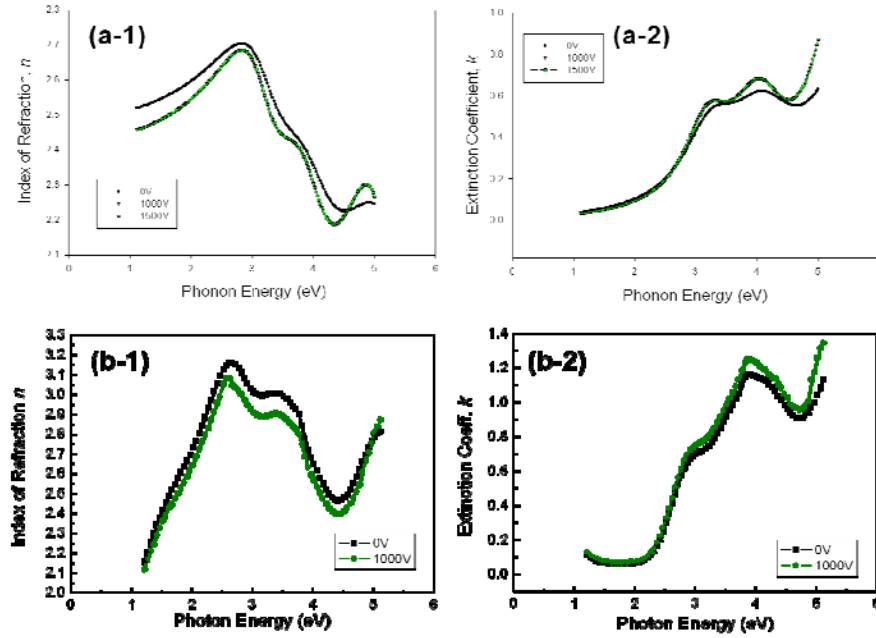
Figure 3. The shifts in refraction index (a-1, b-1) and extinction coefficient of (a-2, b-2) with respect to the applied voltage.

Advanced electrical characterizations were performed using the Hall Effect measurement (HEM) system. The HEM showed the internal carrier dynamics of ScN, including carrier type, bulk carrier density, mobility, resistivity, and conductivity. ScN has the free carrier density of $5.8 \times 10^{20}/cm^3$ and the conductivity of $1.1 \times 10^3/\Omega \cdot cm$. Therefore the background n-type conductivity of as-grown ScN gives enough free electrons that can readily interact with the phonons and applied electric field.

ScN is expected to have an interesting origin of the electro-refractive effect different from that of the classical Pockels effects [11,12]. The valence band of heavy hall in ScN is much shallower at X than that of other materialsm thus the optical transition in ScN comes from second direct bandgap transition at X point instead of Γ point in momentum space. Since the free electron concentration in as-grown ScN film is very high ($\sim 10^{20}/cm^3$), the electron distribution around X point in momentum space is always abundant. On the other hand, the minority carrier-holes, is generated by excitation with a finite minority-carrier life-time, and they are neutralized by recombination. During the short minority-carrier life-time, without the electric field, the majority of hole-population takes place at the top of the valence band, which is at Γ point. When the electric field is applied, the holes are accelerated during the minority-carrier life time and the distribution of holes is affected so that more hole-population can take place at X in momentum space. By bringing more holes toward X point, electrons and holes can make recombination easily without phonons. Therefore, the optical transition at X is enhanced by the electric field. Optical absorption is also affected by the electric field since the generated holes can more easily take the final states near X by the electric field.

The co-sputtered Al and Er in nitrogen/argon atmosphere resulted in a AlN:ErN alloy film with the concentration ratio of 80:20. The bandgaps of AlN:Er3+, AlN:Ho, and AlN:Tb3+ was estimated to be about 5.47eV, 5.18eV, and 5.07eV, respectively as shown in Figure 4. The bandgap energies of AlN:Er3+, AlN:Ho3+, and AlN:Tb3+ are obviously smaller than that of thin film AlN (5.82eV). It is commonly guessed that the impurities introduced into AlN thin films can modulate the local structure and cause the change in optical properties like rare earth doped ScN films.
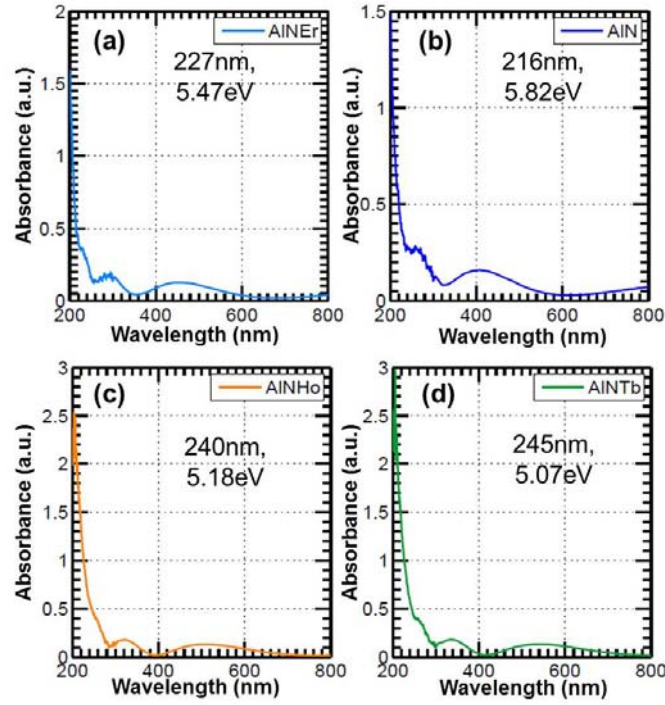
Figure 4. Absorbance (A) as a function of wavelength (λ) for optical band gap calculation of (a) Er-doped AlN, (b) AlN, (c) Ho-doped AlN, and (d) Tb-doped AlN.

Figure 5 shows the measured change in the complex index of refraction (n) and the extinction coefficient (k) of AlN and Er doped AlN with the applied electric field. The refractive index and extinction coefficient of AlN were not changed with respect to the applied voltage. The difference of refractive index and extinction coefficient between generated AlN (without the applied electric field) and experimental AlN (with the applied electric field) is about zero. However the decrease in index of refraction (n) with applied field of Er doped AlN is observed with shift in extinction coefficient (k) as shown in figure 5(b) and 5(c). This sample shows the strongest evidence of possible field induced optical shifts. The non-PTP fit results (b-1 and b-2) show a change in the n and k with applied field. The spectral responses corresponding to the applied fields are much clearer on 4eV to 5eV phonon energy range which is equivalent to UV range. The intensity of refractive index was changed at the visible blue (2.6eV) and green (2.4eV) light, respectively with the applied electric field. The measured amount of change in the refractive index and extinction coefficient of Er doped AlN was relatively large when it was compared with conventional electro-refractive effect (especially, Pockels effect) materials.
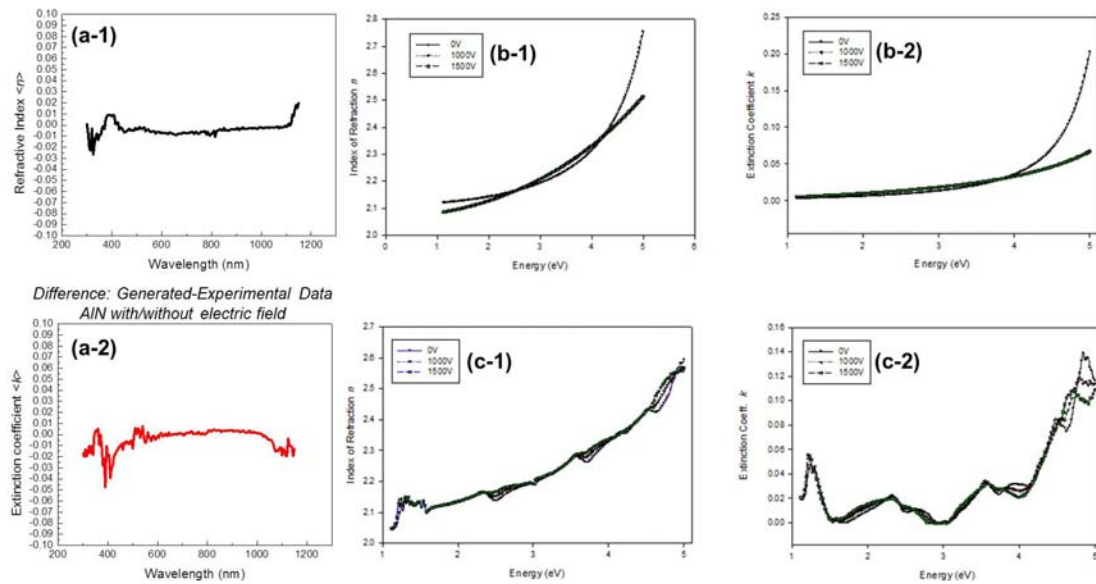
Figure 5. The shifts in refraction index and extinction coefficient of (a-1, 2) AlN, (b-1, 2) and (c-1, 2) AlN doped with Er with respect to the applied voltage. (b-1) and (b-2) show a non-point-to-point (PTP) fit of the tested data. (c-1) and (c-2) show a PTP fit of the tested data.

Summary

By the Stark effects, the quantum level transition within a material can be modified with the applied electric field. The changes in quantum constraint of a material are normally appeared with a pattern of spectral shift and/or refractive index shift. In order to examine the properties of the quantum-confined Stark effect (QCSE), the ScN and AlN doped with rare earth element were developed and tested with electric-field injection. The QCSE may be effectively used for selective spectral transmission in a filtering mechanism by state control through externally applied fields. The reduction in bandgap energy, with dopants, supports the possible multiplicity of energy levels with the orbitals of the dopants. The high density of free electrons and relatively low mobility of ScN film, measured by HEM also indicate that these films contain high level of shallow donors as well as deep levels. The results of thin-film materials based on Er-dopped AlN, Er-doped ScN, and ScN prove that the principle of spectral and refractive index shifts by Stark effects is well-sustained and works very clearly as anticipated and open a new chapter of smart optics technology. ScN, ScN doped Er, and AlN doped Er show a decrease in index of refraction and extinction coefficient over the range 4-5eV with applied electric field. Interestingly, a small amount of spectral shifts appears over the range of 4-5eV. There is also a decrease in the extinction coefficient over this range. From this juncture, the result is very successful and needs further research to discover more materials that show Stark and Zeeman effects over the spectral range covering from IR to UV.

References

[1] W. Franz, Z. Naturforsch., 13 (1958) 484.

[2] L. V. Keldysh, Sov. Phys., JETP7 (1953) 788.

[3] J. D. Dow and D. Redfield, Phys. Rev. B, Solid State, 1 (1970) 3358.

[4] I. A. Merkulov and V. I. Perel, Phys. Lett. A, 45A (1973) 83.

[5] Steinfeld, Jeffrey I., Molecules and Radiation, MIT Press, 1985.

[6] D. C. Hutchings et al., Opt.Quantum Electron. 24 (1992) 1.

[7] M. E. Little and M. E. Kordesch, Appl. Phys. Lett., 78 (2001) 2891.

[8] X. Bai, D. M. Hill, and M. E. Kordesch, Appl. Surf. Sci. 175 (2001) 500.

[9] S. H. Choi and M. E. Little, AIAA Paper, AIAA-2002-5747 (2002).

[10] NASA Langley Research Center C&I Reports by Dr. Sang H. Choi and Dr. Mark Little (2004, 2005, and 2006).

[11] D. K. Shroder, Semiconductor Material and Device Characterization, Second edition, Wiley-Interscience Publication, New York (1998).

[12] D. Gall, M. Städele, K. Järrendahl, I. Petrov, P. Desjardins, R. T. Haasch, T.-Y. Lee, and J. E. Greene, Phys. Rev. B. 63 (2001) 125119.