Journal of Metals, Materials and Minerals. Vol. 13 No. 1 pp. 17-21, 2003.

Quantum Confinement Effect of Alq3/ZnSe Heterostructures

Jiti NUKEAW*

Department Applied Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand

ABSTRACT

The quantum confinement energy in tris(8-hydroxyquinoline) aluminum (Alq3)/ ZnSe heterostructures as single quantum wells (SQW) thin films grown by an e-beam evaporator with a well thickness from 5 nm to 50 nm were investigated by room-temperature photoreflectance (PR) measurements. PR features due to an optical transition energy were observed in the SQWs of well thicknesses. The transition energies were determined by fitting the PR spectra to the theoretical line-shape expression. The transition energy decreased with increasing well thickness due to the increase of the well size in addition to the reduction of quantum confinement energy.

Keywords: Photoreflectance; ZnSe; Alq3; single quantum wells

---

*To whom the correspondence should be addressed:
E-mail address : knjiti@kmitl.ac.th Tel: (662) 326 4341 Ext.330 Fax: (662) 326 4354

INTRODUCTION

The organic light emitting material such as Tris(8-hydroxyquinoline)aluminum(III), Alq3, has been expected to play a significant role in future display technology, since it has a high fluorescence quantum efficiency and semiconductor properties. The Alq3 is used in organic light-emitting diodes (OLEDs) as an electron transport material and emitting layer. The unique structural characteristics of the organic and inorganic materials provide for equally interesting and potentially useful physical properties. For example, thermal evaporation of amorphous multilayers of copper pthalocyanine (CuPc) and TiO_2, with a periodicity of 5 nm forms a composite material with a modulated electronic structure analogous to that of type-II quantum well structures (Takada, *et al.* 1992; and Takada, *et al.* 1995). The physical properties of the organic and inorganic quantum well structure is a two-dimensional quantum confinement effect due to the large difference in the band gaps and the dielectric constants between layers.

Modulation spectroscopy is an important technique for the study and characterization of energy-band structures of semiconductors. Modulation techniques such as electroreflectance (ER) and photoreflectance (PR) are particularly useful since they yield spectra with sharp features at the critical-point energies. The features in the spectra appear at energies corresponding to the band gap characteristic points or other peculiarities in the dielectric function. PR is of considerable interest because it is contactless, requires no special mounting of the sample, can be performed in a variety of transparent ambients, and is sensitive to surface and interface electric fields (Nukeaw, *et al.* 1997; and Nukeaw, *et al.* 1998). Reddy, *et al.* (1987) have reported PR results on GaAs/(Al,Ga)As multiple quantum wells of different well thicknesses. Their results were concerned with transitions involving the so-called 'unconfined' states. Furthermore Reddy, *et al.* (1987), they have performed PR studies on a series of InGaAs/GaAs single quantum wells (SQWs) of different well thicknesses in the range from 80 Å to 120 Å.Their study indicated that the conduction-band discontinuity is 0.420 eV. Yaguchi, *et al.* (1993) have studied the band offsets at the hetero-interface $GaAs/GaAs_{1-x}P_x$ SQWs structures of different well thicknesses in the range from 50 Å to 200 Å using PR. The band offsets were found to be almost linearly dependent on the phosphorus composition in the range of $x < 0.23$. However little research with respect to PR studies on organic and inorganic SQW structures has been reported.

In this report, we investigated the optical transition energy of Alq3/ZnSe heteostructures as SQW with well thickness from 5 to 50 nm by PR measurements.

EXPERIMENTS

The samples were prepared using a high vacuum multi-pocket electron-beam evaporator (Edwards AUTO306). The film thickness was measured by x-tal as a thickness monitor (Edwards FTM7). A 200 nm ZnSe buffer layer was grown on glass substrates at room temperature, followed by Alq3 layers with varied thickness from 5 nm to 50 nm, and a 200 nm ZnSe cap layer, respectively. The Alq3 bulk sample with thickness of 1 μm was used as a reference.

In our PR measurements, a modulation light was provided by a 442 nm 5 mW He-Cd laser. The chopped laser light was irradiated onto the sample with a spot radius of about 1 mm. The chopper frequency is 400 Hz. A 100 W tungsten lamp was dispersed by a 25 cm monochromator and used as a probe light. The reflected probe light from the sample was detected by an Si detector, and the signal from the detector was fed to a lock-in amplifier.

RESULTS AND DISCUSSION

A scanning electron micrograph (SEM) obtained on a nanocrystalline ZnSe surface is shown in Figure 1, while an atom force micrograph (AFM) image obtained on Alq3 as small-molecular thin films are shown in Figure 2, respectively.

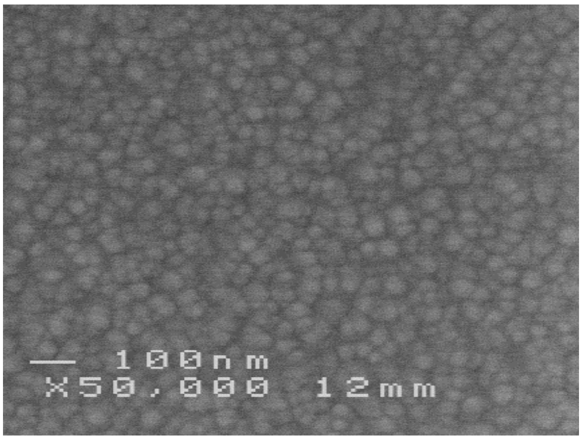

Figure 1 A SEM obtained on nanocrystal-ZnSe surface.

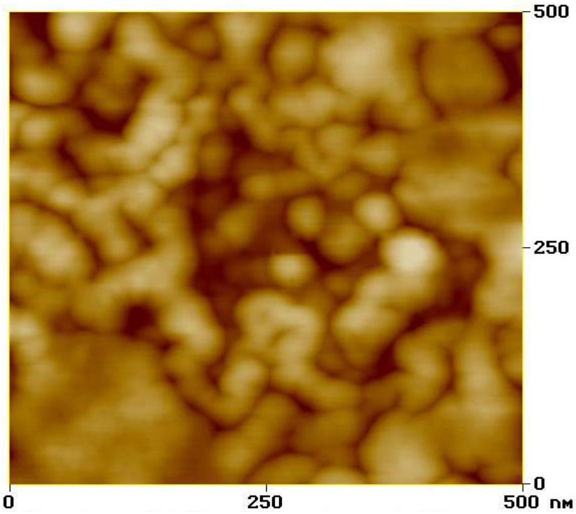

Figure 2 AFM images obtained on small-molecular Alq3 thin films.

The PR spectrum of bulk alq3 is shown in Figure 3, while PR spectra of all the samples are shown in Figure 4. The transition energies from the Alq3 well are observed. The PR spectrum of the bulk alq3 is similar to that of 50 nm SQW.

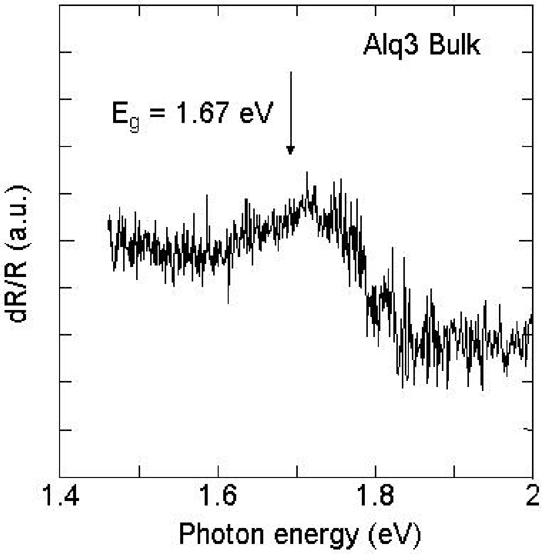

Figure 3 Room-temperature PR spectra of bulk alq3 sample.

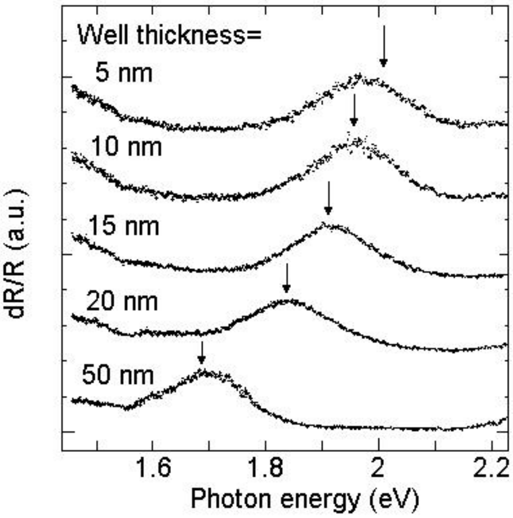

Figure 4 Room-temperature PR spectra as a function of the well thickness. The transition energies determined by the fittings are indicated by arrows.

The PR spectra as a function of photon energy can be analyzed using the familiar Aspnes third-derivative function in the low electric field limit Aspens (1973), i.e.,

$$\frac{\Delta R}{R} = \mathrm{Re}\sum_{j=1}^{p} C_j e^{i\theta_j}(E - E_{gi} + i\Gamma_j)^{-n} \quad (1).$$

Here, R is the reflectance, ΔR is the induced change in the reflectance by modulation light, E is the photon energy, p is the total number of spectral structures to be fitted $\boldsymbol{E}_{gi}, \Gamma_j, \boldsymbol{C}_j$ and θ_j are transition energy, broadening parameter, amplitude and phase, respectively, of the feature corresponding to the jth critical point. The parameter n is a factor used to specify the critical point dimension.

The energy level associated with transition energy was determined by least-square fitting of Eq. (1) to PR spectra obtained experimentally. In this calculation, the n value is 3 for the quantum well transiton feature (Misiewicz, *et al.* 1994; and Basmaji, *et al.* 1990). The transition energy obtained from these fittings as a function of the well thickness is shown in Figure 5. The transition energy decreased with increasing well thickness.

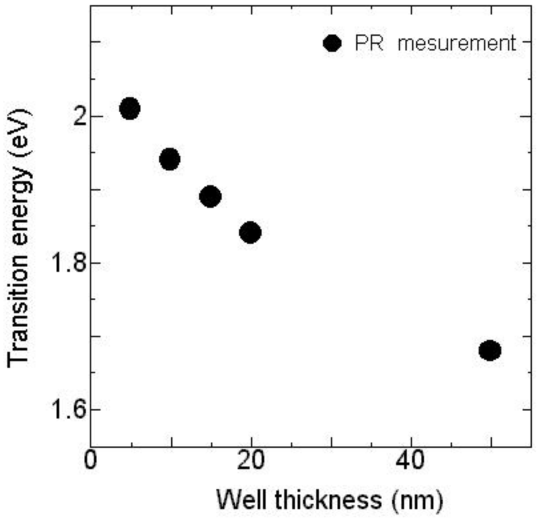

Figure 5 Dependence of transition energy on well thickness.

Huang, *et al.* (1998) reported for the first time organic multiple-quantum-well-like electroluminescent (EL) devices fabricated by the doping technique. The EL device consists of N,N′-Bis(3-methyphenyl)-N,N′-diphenylbenzidine used as a hole transporter, undoped Alq3 as a barrier potential or an electron transporter, and Alq doped with 5,6,11,12-tetraphenylnaphthacene as a potential well and a light emitter. The quantum confinement effects of well width and well number on EL device properties was demonstrated. Tokito, *et al.* (1994) reported that a new class of superlattice materials consisting of alternating layers of organic and inorganic materials has been prepared from Alq3 and MgF_2 by vacuum deposition. The Alq3 layer thickness in the superlattices was varied from 10 to 50 Å. From the optical absorption and photoluminescence measurements, it was found that the exciton energy shifts to higher energy with decreasing Alq3 layer thickness. The changes of the exciton energy could be interpreted as the confinement effects of exciton in the Alq3 thin layers.

The electronic structure of the conduction and valence bands of ZnSe have been measured to be at –4 and –6.7eV below the vacuum level. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of Alq_3 are at –4.8 and –6.4 eV, respectively (Mason, *et al.* 2001). From the configuration and the energy band diagrams, the structure was like an inorganic quantum well structure, so conveniently, it was called an organic-inorganic quantum well structure, where ZnSe acts as a barrier potential and Alq3 as a potential well. The transition energy decreases with increasing thickness might be due to the increase of well results in the reduction of quantum confinement energies. A decrease in the size should affect the properties of the film. The properties of larger size film should be similar to that of the bulk where the effect of quantum confinement is small.

CONCLUSIONS

PR measurements were used to investigate optical transition energies in ZnSe/Alq3/ZnSe SQWs with a well thicknesses from 5 to 50 nm grown by an electron-beam evaporator. The PR spectra showed the optical transition energy in the SQWs. The transition energy was determined by fitting the PR spectra to the theoretical line-shape expression. The optical transition energy decrease with an increasing thickness might be due to the increase of well size in addition to the reduction of quantum confinement energy.

ACKNOWLEDGMENTS

We would like to acknowledge the National Electronics and Computer Technology Center (NECTEC), Thailand for the research grant and Faculty of science, King Mongkut's Institute of Technology Ladkrabang Thailand for the research facilities. This work was supported in part by the scientific research and development No. NT-B-06-4A-22-314 from NECTEC.

REFERENCES

Aspnes, D. E. 1973. *Surf. Sci.* **37** : 418.

Basmaji, P., Ceschin, A. M., Li, Siu M., Hipolito, O., Bernussi, A. A., Iikawa, F. and Mostisuke, P. 1990. *Surf. Sci.*. **228** : 356.

Hang, J., Yang, K., Xie, Z., Vhen, B., Jiang, H. and Liu, S. 1998. *Appl. Phys. Lett.* **7** : 3348.

Mason, M. G., Tang, C. W., Hung, L.-S., Raychaudhuri, P., Madathil, J., Giesen. D.J., Yan, L., Le, Q.T., Gao, Y., Lee, S.-T., Liao, L. S., Cheng, L. F., Salaneck, W.R., dos Santos, D. A. and Bredas, J.L. 2001. Interfacial chemistry of Alq(3) and LiF with reactive metals. *J. Appl. Phys.* **89 (5)** : 2756-2765.

Misiewicz, Y., Markeiwicz, P., Rebisz, J., Gumienmy, Z., Penek, M., Sciana, B. and Tlaczala, M. 1994. *Phys. Stat. Sol.* (B) **183** : 143.

Nukeaw, J., Fujiwara, Y. and Takeda, Y. 1997. Observation of electric fields at surface and interface of doped GaAs semi-insulating GaAs structures by fast fourier transformed photoreflectance. *Jpn. J. Appl. Phys.* **36 (11)** : 7019-7023.

Nukeaw, J., Fujiwara, Y., Takeda, Y., Funato, M., Aoki, S., Fujita, Sz. and Fujita, Sg. 1998. Observation of high electric field at ZnSe/GaAs heterointerfaces by fast fourier transformed photoreflectance. *Thin Solid films.* **334 (1-2)** : 11-14.

Reddy, U. K., Ji, G., Henderson, T., Huang, D., Houdre, R. and Morkoc, H. 1989. *J. Vac. Sci. Technol.* **B7** : 1106.

Reddy, U. K., Ji, G., Henderson, T., Morkoc, H., and Schulman, J.N. 1987. *J. Appl. Phys.* **62** : 145.

Takada, J. 1995. *Jpn. J. Appl. Phys.* **34** : 3864.

Takada, J., Awaji, H., Koshioka, M., Nakajima, S. and Nevin, W.A. 1992. *Appl. Phys. Lett.* **61** *:* 2184.

Tokito, S., Sakata, J. and Taga, Y. 1994. Structures and optical-properties of organic-inorganic superlatices. *Appl. Phys. Lett.* **64 (11)** : 1353-1355.

Yaguchi, H., Zhang, X., Ota, K., Nagahara, M., Onabe, K., Sjoraki, Y. and Ito, R. 1993. *Jpn. J. Appl. Phys.* **32** : 544.

(Revised version accepted October 13, 2003)