Electron Affinity Control of Zinc Silicon Oxide Nanoparticles for Electron Transport Layer in OLEDs and QLEDs

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Keywords: nanoparticles, inorganic ETL, inkjet printed OLED, quantum dot light emitting diode.

ABSTRACT

Nanoparticles of transparent semiconducting zinc silicon oxide, with diameter below 4 nm, were found to exhibit a variety of electron affinity ranging from 3.6 eV to 2.7 eV, by altering Si content. Resulting nanoparticles can be dispersed in glycol solvents, showing a good surface flatness in the spin-coated films.

1 Introduction

The tuning of electron affinity, EA, of electron transport layer, ETL, is important for the efficient electron carrier injection into the light emitting layer, EML, such as quantum dots, QDs, or light emitting organic materials.

Sputter-deposited film of zinc silicon oxide, ZSO, is suitable for the above ETL applications from viewpoint of EA control [1-2].

In this work, we demonstrate a novel oxide material (ZSO nanoparticles) as a candidate for printed ETLs, in which EA can be adjusted to EA or LUMO of EMLs. The main feature of ZSO nanoparticles is that EA can be controlled by Zn:Si composition, without any surface modification by using organic ligands. In our opinion, the organic ligands are not always vigorous against the printable environment such as ink solvents. Requirements on printable ETLs and our material design are described as follows.

1.1 Requirements and Material Design

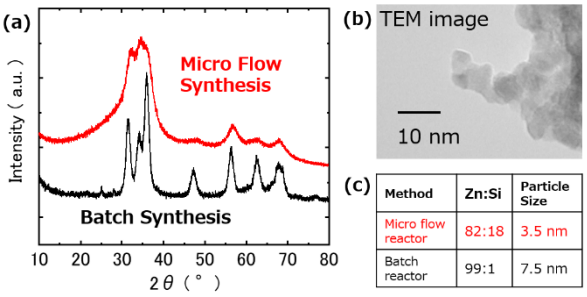
(1) Diameter below 4 nm; if it is >4nm, the printed film will have worse flatness. On the contrary, in case of the smaller diameter such as <2nm, there should be unstable band gap energy due to quantum effect. Liquid phase synthesis is also unstable because the particle size is close to the critical radius of homogeneous nucleation.

(2) Range of nanoparticle's EA covers different EMLs, i.e., the range between 3 and 4 eV is favorable.

(3) The above EA is controlled not by the surface dipole of the organic ligands nor quantum effect that needs very precise particle size control, but the atomic structure of the nanoparticle, i.e., EA is controlled by the compositional effect.

(4) Si was chosen as an additive element, since SiO_2 is more stable against acid or alkali, as compared to ZnO. ZSO is chemically more stable than pure ZnO.

(5) To achieve the above requirement, we employed a buildup synthesis of double oxide in liquidus phase not by using conventional batch synthesis but by using a micro flow reactor, for the purpose of coping with electrical property such as EA and small particle size of <4 nm.



Method	Zn:Si	Particle Size
Micro flow reactor	82:18	3.5 nm
Batch reactor	99:1	7.5 nm

Fig. 1 Comparison between micro flow and batch synthesis, (a) XRD pattern, (b) TEM image, (c) Zn:Si ratio by SEM-EDX.

2 Experiment

Zinc acetate and TEOS were used as raw materials for Zn and Si, respectively. Both reagents were dissolved in DMSO solvent in a specific ratio. The resulting precursor solution was mixed with organic alkali by using a micro flow reactor, expecting the formation of double oxide, via dehydration and condensation of hydroxide monomers such as $Zn(OH)_2$ or $Si(OH)_4$. For comparison, the same precursor solution and the organic alkali were mixed in a beaker (batch synthesis), where the solution was kept stirred during the whole reaction.

After the synthesis, the nanoparticles were precipitated in poor solvent and treated with centrifugal separation & solvent replacement (washing procedure), in order to obtain clean surface. The nature of clean surface was confirmed by checking the change in the cutoff energy of ultraviolet spectra being less than 0.05 eV [3], before and after the Ar+ ion sputtering. After the washing procedures, dry powders were subjected to XRD and FT-IR measurement. The particle diameter was determined by using TEM and Scherrer radius by XRD. Dispersion liquid was fabricated by using propylene glycol, PG, with monoethanolamine, MEA, additive as a solvent. The dispersion liquid was treated by ultrasonic homogenizer. PG was chosen as an

example for a polar solvent. Optical absorption was measured by using liquid micro cell, having an optical length of 1 cm. Optical band gap, Eg, was derived by using Tauc's relation. Ultraviolet photoelectron spectra, UPS, were measured for the spin-coated films, to observe ionization potential, IP, and work function, ϕ. Electron affinity, EA, was calculated by using equation, EA = IP – Eg, while the consistency and reliability of UPS measurements were checked by referring IP and ϕ. In the preliminarily experiments, we confirmed that MEA does not seriously affect the observed value of work function and ionization potential.

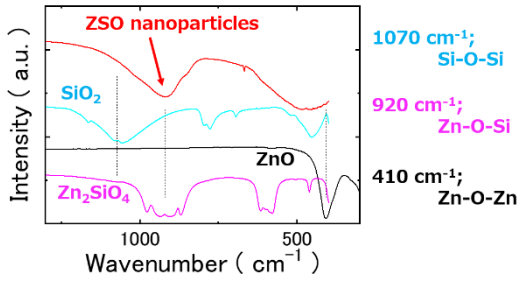


Fig. 2 FT-IR spectra observed for ZSO nanoparticles, along with SiO_2 (alpha Quartz), ZnO (Wurtzite), Zn_2SiO_4 (Willemite) for reference.

3 Results

The nano-meter-sized particles were successfully obtained by micro flow reactor, while the batch synthesis did not provide Si-containing products. The Si content by micro flow reactor reached as large as 18%, apparently exceeding solubility limit in bulk ZnO wurtzite, although the nanoparticles remain in the wurtzite-like structure by XRD (Fig.1). The FT-IR spectra showed the resulting zinc silicon oxide, ZSO, nanoparticles have Zn-O-Si bonding, which is totally different from pure ZnO from viewpoint of local atomic arrangement (Fig.2).

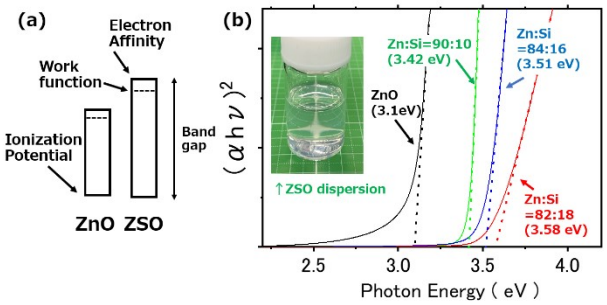


Fig. 3 Comparison of ZnO and ZSO, (a) Energy band diagram, (b) Tauc's plot (direct allowed transition) of Optical absorption spectra for dispersion liquid of ZSO nanoparticles with different Si content. Inset shows the appearance of the sample with Zn:Si=90:10.

Fig.3 shows the band gap widening in ZSO particles, that is clearly accompanied by an increase in Si content. In addition, we found ZSO particles are well dispersed in PG + MEA solvent. The RMS of the spin-coated film was < 2nm. UPS measurements revealed the EA change is dominated by Zn:Si rather than particle size as shown in Table 1.

4 Discussion

In comparison with conventional liquid phase synthesis, the main feature of micro flow synthesis is better efficiency in the mixture of raw materials. In other words, at the present chemical system, at least one of the elementary reactions is diffusion limited.

EA control was successfully observed for ZSO nanoparticles, in which the clean surface was experimentally ensured. The controllability does not depend on specific surface modifier such as organic ligand, meaning extensive choice of solvents, i.e., the ETL ink will be more compatible with QDs' ligands, those are indispensable for functionalities of QDs.

The observed work function indicates that Fermi level is just below the conduction band, implying n-type semiconducting behavior of ETLs formed by ZSO nanoparticles.

Table 1 Electron Affinity, EA, of ZSO nanoparticles deduced from Ultraviolet photoelectron spectra .

Zn:Si	Particle Size (nm)	EA (eV), ϕ in ()	Band Gap (eV)
ZnO	12	4.0 (4.4)	3.10
90:10	3.8	3.6 (3.8)	3.42
84:16	3.8	3.2 (3.6)	3.51
82:18	3.5	2.7 (3.2)	3.58

5 Conclusions

By using micro flow reactor, novel double oxide compound, ZSO nanoparticles were successfully fabricated. Spin-coated film of ZSO nanoparticles showed good flatness of <2nm, via the dispersion liquid using glycol and MEA solvent. ZSO nanoparticles were found to be transparent n-type semiconductor. Electron affinity can be controlled by utilizing compositional effect of Zn:Si, not by relying on organic ligands, leading to better chemical stability and compatibility, implying the present material is a good candidate for printable ETLs.

References

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