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VAN DER WAALS DRIVEN SELF-ASSEMBLY APPROACH FOR ZnS NANOPARTICLES

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Abstract: Thin film nanoparticles have been prepared on glass substrate by spin coating and self-assembly method. Combination techniques were used to study on structural thin film using Field Emission Scanning Electron Microscopy (FE-SEM) and the elements were confirmed using Energy Dispersive X-Ray (EDX). The results of this experiment showed that the well-organized nanoparticles were produced with the size of nanoparticle 30-50 nm. EDX analysis confirmed the ZnS nanoparticles with percentage of Zn = 24.9% and S = 0.6 %. Using Van der Walls equation, formation of larger size of nanoparticles influence strong result in van der Waals relation between particles. This outcome can be used to develop nanomaterials in the future.

Keywords: *Structure of thin film, van der Waals, self-assembly, ZnS nanoparticles, sol gel method*

Introduction

Nanophotonic crystals have extraordinary potential especially in optoelectronic devices. They have been incorporated in phosphor, sensor, and waveguide application because they are able to enhance the efficiency of existing technology (Chiappini *et al.,* 2011). Recently, different nanophotonic crystals have been fabricated using various materials such as ZnS, CdS, and ZnO (Ali *et al.*, 2014; Vettumperumal *et al.,* 2013). Self-assembly is a fundamental mechanism and is one of the current popular topics in the field of material research. In simple understanding, self-assembly is a mechanism in which different nanoparticle assembly motifs of even close-packed periodic structures form in materials through spatial arrangement of their fundamental building blocks. Directed self-assembly of nanoparticles refers to the process whereby an intrinsically self-assembling system is aided or modulated using directing agents, external fields, or templates (Marek *et al.*, 2010). Basically, it is much easier to produce nanocrystal-based photonic crystals using modern directed self-assembly fabrication techniques such as etching process (Orloff *et al.,* 1992; Yun *et al.,* 2004), but these techniques are very costly. Therefore, researchers are trying to discover simpler and cost-friendly alternative techniques to produce cost-friendly crystal such as self-assembly approach using spin coating, dip coating, chemical bath deposition, chemical vapor deposition and hydrothermal (Mohd *et al*. 2012).

Previous research shows that good morphology of ZnO:Mn nanoparticles was produced using hierarchical and self-assembly method (Hao *et al.*, 2012). In this process, forces that control self-assembly are determined by competing noncovalent intramolecular or intraparticulate interactions meanwhile the hierarchical structures obtained through the self-assembly of nanocrystalline building blocks provide new opportunities for optimizing, tuning and/or enhancing the properties and performance of the materials. Other research have developed ZnS:Mn nanocrystal using spin coating and self-assembly approach (Noor *et al.,* 2014). Directed self-assembly method was employed to align the nanocrystal in a single layer plane while metal tape was used during spin coating process to prevent ZnS:Mn sol from being splashed out of the boundary line. After undergoing annealing process at certain temperature, a homogeneous nanocrystal was formed but the factors that influence the alignment of nanocrystal were not addressed.

Therefore, the current project considers all possible factors and would suggest the significant factors that affect the arrangement of ZnS nanocrystal. Several studies have highlighted temperature as one of the significant factors. Using atomistic models, Dean *et al.* (2006) simulated the crystallization of other mesoporous materials at different temperatures to complement their existing experimental studies. Their simulation suggested that nanoparticles self-assemble and form an amorphous mesoporous framework while they crystalize at low temperatures. Experimental results verified this simulation. Molecke (2011) simulated the formation of nano-wires during a drying process using multiscale modeling approach. This simulation showed that the linear structures were formed by lowering the maximum force that the particles could exert on each other and by increasing the solvent viscosity. The reason behind this combination was explained using a mechanical model. Li *et al.* (2013) reviewed the relationship of the nanocomposites formed from nanoparticles with different properties. They concluded that the interaction between the nanoparticles and the polymers, the long-range forces (Van der Waals or electrostatic) between particles, the size and shape of nanoparticles, and the composition and molecular architecture of the polymers affect the self-assembly process and affect the nanocomposites. In this project, we have produced ZnS nanoparticles via spin coating and self-assembly method, characterized and analyzed the impact of directed self-assembly method approach during spin coating process.

Materials and Methods

ZnS solution was prepared using sol gel method using zinc acetate dihydrate, thiourea, ethanol and distilled water. In the sol gel process, zinc acetate dihydrate were dissolved in ethanol and distilled water and stirred for 3 days. After that, ZnS sol was deposited on glass substrate using mechanical spin coater (GLICHN Technology T-108 Spin Coater) at the speed of 2000 rpm for 20 s. During the spin coating process, metal tape was used to prevent ZnS:Mn sol from being splashed out of the boundary line as shown in Figure 1. This step is referred to as self-assembly technique. Then the thin film was annealed at 400 ˚C for 2 hours. The structure of thin film nanoparticles coated with gold then was characterized using Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray (EDX) model: Supra 55VP.

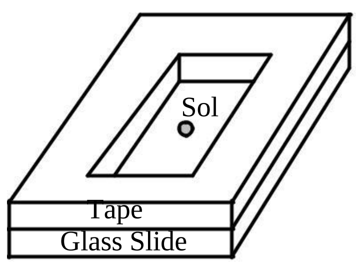

Figure 1: Metal tape as a barrier to avoid solution from being splashed out of the glass substrate. It is the traditional method to produce nanocrystal in well aligned.

Results and Discussion

Figure 2 shows FE-SEM image that captured the structure of thin film at vicinity of tape area consisting nanoparticles that were arranged in an organized manner with size ranging from 30 nm to 50 nm. Thin film with such structure could be formed owing to the support provided by the metal tape during the spin coating process. A typical spinning process at 2000 rpm expels fluid from glass slide or substrate as fluid moves outwards in radial direction. The metal tape prevented the sol from being splashed out from glass slide or substrate as fluid moves outwards in radial direction. The metal tape prevented the sol from being splashed out from glass slide allowing more nanoparticles to remain intact on substrate. At the same time, the metal tape is also an enabler of self-assembly process that organizes the position of nanoparticles.

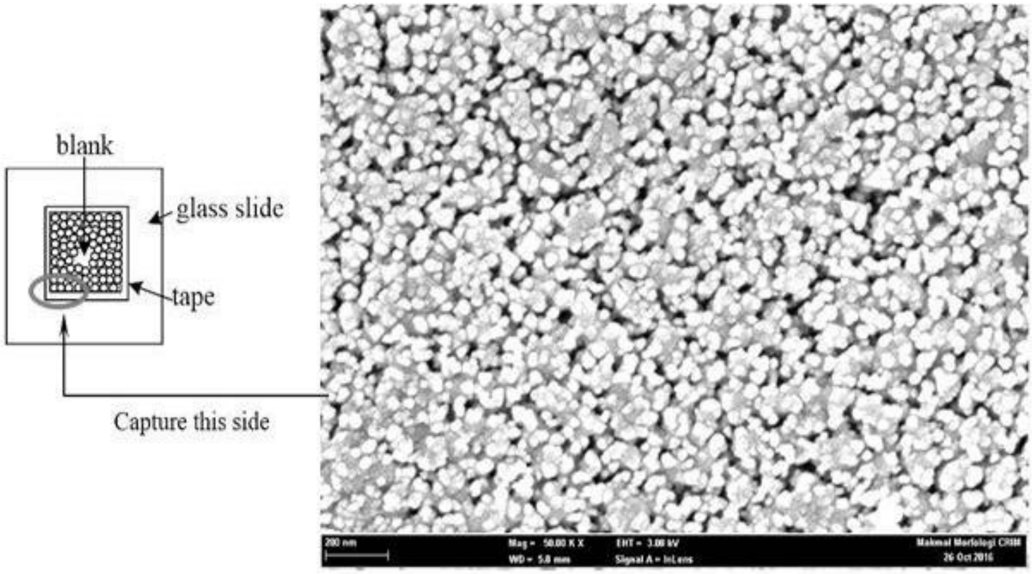

Figure 2: Field Emission Scanning Electron Microscopy (FE-SEM) Image using 50,000X magnification and 3 kV voltage: After spin coating process and annealing process within 120 minutes.

Figures 3 shows the forces that act on sol during any spin coating process. When the fluid covers the surface of substrate, the excessive fluid will spill over the edges in an unpredictable manner leaving a thin uniform layer on the surface with geometry resembling the shape of fingers (de Bruijne *et al.,* 1999). Mihael (2009) explained that the movement of fluid in terms of wave motion on substrate that does not have any border surrounding the fluid would rupture during the spinning process. The flow with contact lines tends to form thin film with shape of finger. With metal tape, the fluid would flow radically in a more consistent manner.

The outcome from this experiment can be related to the Van der Waals theory which is more dominant compared to other interparticle forces such as electrostatic force. Van der Waals force between nanoparticle (D<<R) is described as

$$F_{vdw} = -\frac{A_H R}{12} \qquad \textbf{Eq. 1}$$

Where R is radius, A_H is Hamaker constant and D is the minimum interparticle distance.

The Hamaker constant is calculated using the equation

$$A_H = \frac{3}{4} k_B T \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^2 + \frac{3hv_e}{16\sqrt{2}} \frac{\left(n_1^2 - n_2^2\right)^2}{\left(n_1^2 + n_2^2\right)^{3/2}} \qquad \textbf{Eq. 2}$$

Where T is absolute temperature, K_B is Boltzmann's constant, h is Plank's constant, ve is UV adsorptive frequency, n_1 is the index of refraction of agglomerates, ε_1 is the dielectric constant of agglomerates, n_2 and ε_2 are the index of refraction and dielectric constant of fluid, respectively. There is a direct relationship between the Hamaker constant and the temperature (Ali, 2015). Hamaker constants for cubic ZnS and hexagonal ZnS are 4.80 and 5.74, respectively (Bergström, 1997; 2001).

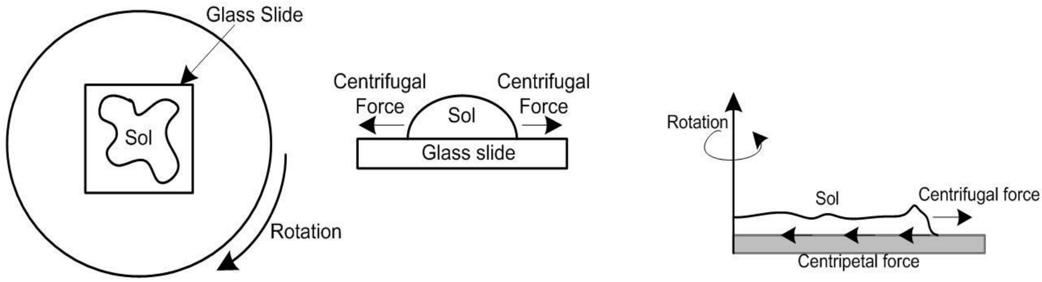

Figure 3: Drop of liquid on spinning plate and schematic image on rotating drop in the radial direction

There are four stages in the spin coating process: deposition, spin-up, stable fluid outflow and evaporation. During the stage of stable fluid outflow, the sol is uniformly distributed. Regardless of its level of viscosity, the radial flow of fluid will eventually dampen as the coating thickness shrinks (Sahu *et al.*, 2009). In this situation, Van der Waals force induces the spontaneous self-assembly of particles. During the assembly process, the particles tend to aggregate or associate with other particles. Figure 4 and Figure 5 illustrate the relationship between Van der Waals force with separation between nanoparticles using the particle size ranging between 20 nm and 80 nm, and with radius. It can be seen that, Van der Waals force plays an important role in producing thin film nanoparticles whether in spinning process and self-assembly process. Figure 4 demonstrates that the Van der Waals force decrease with the increase of the separation between nanoparticles. In fact, by decreasing separation between particles, the particles have higher tendency to attract to each other.

Apart from that, formation of larger size of nanoparticle increases the Van der Waals force between particles as shown in Figure 5. The size of nanoparticles is dependent on the speed employed in the spinning process. The speed affects the degree of centrifugal force applied to the sol. Hence, speed spin could indirectly reflect the final thickness formed on the substrate which could be defined as nanoparticle size. Sahu *et al.* (2009) indicated that minor variations of ±50 rpm in spinning process could result in thickness change of 10%.

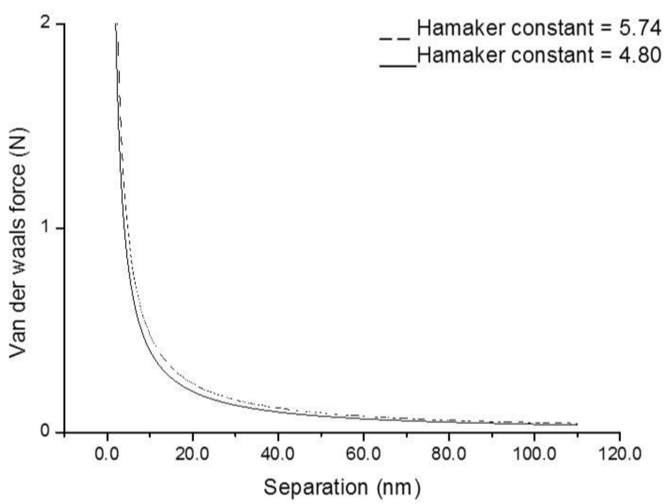

Figure Figure 4: Van der Waals force depending on separation between nanoparticles

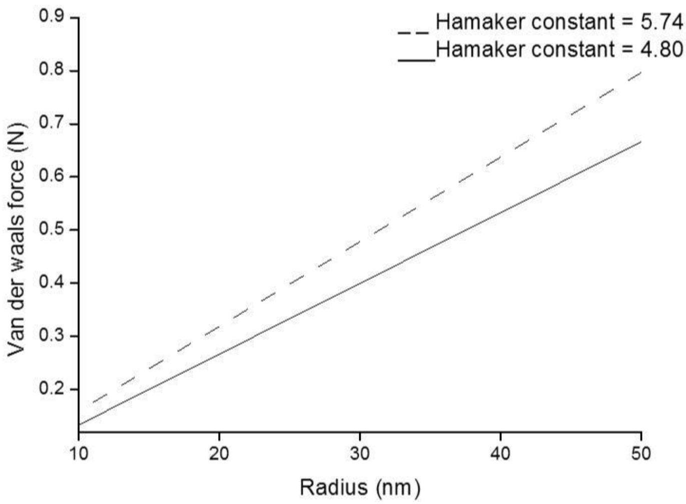

Figure 5: Van der Waals force depending on radius of nanoparticles. Assume 50 nm in radius is larger particle which can consider in nano range.

Figure 6 shows the EDX result of ZnS thin film with percentage of Zn, S, Si, and O is 24.0%, 0.6 %, 35.2 % and 39.1 %, respectively. Element of Si and O were detected due to glass slide and air. Hence, it is confirmed that the thin film contains of ZnS nanoparticles.

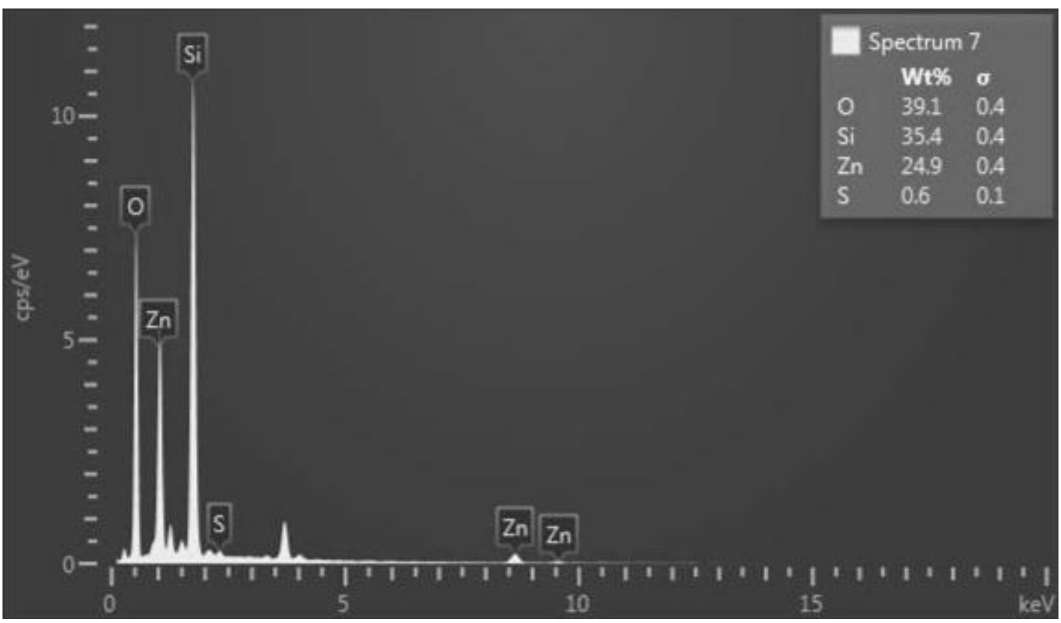

Figure 6: EDX result of ZnS thin film with proportion element measured.

Conclusion

In this project, we have analyzed the impact of directed self-assembly method approach during spin coating process. Outcome from this experiment showed that the well-organized nanoparticles were produced with the size of nanoparticles 30-50 nm and ZnS thin film was confirmed by EDX analysis. It is suggested that the method is influenced by van der Waals force during spinning process. It showed that the force increases with the increase of nanoparticle size and decrease of separation between nanoparticles. In the future, certain types of interparticle repulsion need to be introduced to overcome the van der Waals attraction to ensure a more stable system. This study can be used to make prognostication about nanoparticle arrangement for upcoming research.

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