Growth mechanism of chemically prepared ZnO-SiO$_2$ nanostructures grown on glass and silicon substrates

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Abstract. Different surface morphology of ZnO-SiO$_2$ has been successfully grown on glass and silicon substrates using chemical bath deposition method. The dependence on the substrates used on the morphology of ZnO-SiO$_2$ was investigated. The morphology of ZnO-SiO$_2$ on glass substrate was flake-like in form and changes to protruding hemispherical structures when grown on silicon substrate. Elemental composition analysis verified the presence of ZnO and SiO$_2$. Infrared characteristics showed an absorption band for the binding of ZnO and SiO$_2$ and revealed the presence of zinc complexes. We proposed a mechanism on the growth of ZnO-SiO$_2$ on glass and silicon substrate using low temperature deposition technique.

1. Introduction
Among inorganic semiconductors, zinc oxide (ZnO), having a wide band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV, attracted much attention and candidate for many applications such as gas sensors [1], optical wave guides [2], solar cells [3] and SAW ultraviolet photodetectors [4]. Because of these applications, many growth techniques have been used for deposition of ZnO nanostructures and these include sputtering [5], chemical vapor deposition [6], pulsed laser deposition [7], chemical bath deposition [8], atomic layer deposition [9], spray pyrolysis [10] and molecular beam epitaxy [11]. Although ZnO has many optoelectronic applications, it has also its limitations such as its high catalytic activity that may degrade its functions. To overcome its limitations, a concept of composite material is done. Among ZnO-based composite materials, ZnO-SiO$_2$ is gaining much attention due their compatibility and stability. There are existing works in the synthesis of ZnO-SiO$_2$, however, most of the processes involve sophisticated and expensive method like double jet precipitation [12-13], hydrolysis method [14], sonochemical synthesis [15], and spray drying [16]. Studies conducted by references [17-19] were able to synthesized ZnO-SiO$_2$ in where they used tetraethoxysilicate (TEOS) as a source of SiO$_2$ which is toxic chemical and very expensive. However, a technique called chemical bath deposition is extremely attractive for the synthesis of ZnO-SiO$_2$ due to its advantageous features such as it is a low temperature and low cost technique, easy coating of large surfaces and the growth conditions can be easily controlled. Aside from this, there is no current work on the synthesis of ZnO-SiO$_2$ through chemical bath
deposition method deposited on glass and silicon substrates using silica obtained from rice husk ash (RHA). RHA is considered as a waste material in the locality.

In this work, low temperature chemical bath deposition method is used for the synthesis of ZnO-SiO$_2$. The growth mechanism on flake-like and hemispherical formation of ZnO-SiO$_2$ on glass and silicon substrates is proposed. Detailed analysis on surface morphology and infrared characteristics of ZnO-SiO$_2$ is done and effect of OH$^-$ concentration to the growth of ZnO-SiO$_2$ is also discussed.

2. Experimental

2.1 Preparation of the substrates

The substrates are cleaned first before the deposition process. The silicon substrates with dimension of 1.5 cm x 1.5 cm were first washed with distilled water. These substrates were soaked with ethanol then rinsed with distilled water. After that, they were immersed in ethanol and washed again by distilled water. Each step is done for every 5 minutes for three times. After cleaning, silicon substrates were dried in air. The amorphous glass substrates (25.4 mm x 76.2 mm) on the other hand were thoroughly cleaned using acetone, ethanol, hydrochloric acid and distilled water. The glass substrates were first immersed in acetone swaying the substrates 24 times. It is then followed by degreasing the substrates using distilled water and then immersed in ethanol and again rinsed with distilled water. The amorphous substrates were washed by 1.0 M hydrochloric acid and completely degreased with distilled water. These methods were performed three times. The glass substrates were dried in ambient air condition.

2.2 Synthesis and characterization of ZnO-SiO$_2$

ZnO-SiO$_2$ composite was deposited on silicon and glass substrates through chemical bath deposition method using laboratory grade chemical reagents. A 3.0 M ammonium hydroxide (NH$_4$OH) and 0.03 M zinc sulphate heptahydrate (ZnSO$_4$·7H$_2$O) were used to form the aqueous bath solution. Silica (SiO$_2$) powder from RHA was added to the aqueous solution and the resulting mixture was magnetically stirred at 360 rpm for 30 minutes and heated up to 70°C using magnetic stirrer with hot plate apparatus. After 30 minute of stirring, the substrates were immersed in the prepared solution and again magnetically stirred for five hours. After the deposition, the substrate was rinsed with heated deionized water and dried at room temperature.

The surface morphology and elemental composition of the ZnO-SiO$_2$ composite was observed using scanning electron microscopy-energy dispersive X-ray (SEM-EDX) using JEOL M-6510LA analytical scanning microscope. The functional groups (chemical bonding) and impurities present in the samples were investigated by Fourier transform infrared (FTIR) spectroscopy using Perkin Elmer Spectrum 100 FTIR spectrometer with scanning range of 600-4000 cm$^{-1}$.

3. Results and Discussion

3.1. Surface Morphology

Figure 1(a) shows the SEM image of ZnO deposited on glass substrate. It is apparent in the figure that flake-like formations were deposited on glass substrates. This formation of flake-like structures is attributed to the excess OH$^-$ ions which are responsible for the convolution of Zn$^{2+}$ ions forming flake-like structure than sea urchin like ZnO.

Figure 1(b) is the surface morphology of ZnO-SiO$_2$ which also shows flake-like structures that is larger in size compared to the flake-like formation of ZnO alone. This formation is due to the amorphous nature of the glass substrate used and to the excess OH$^-$ ions that facilitates faster nucleation of the Zn(OH)$_2$ seed nuclei. In an amorphous glass substrate, many phase boundaries act as nucleation sites. At the nucleation sites, the effective surface energy is lower, thus diminishing the free energy barrier and facilitating faster nucleation. The Zn(OH)$_2$ formed must have attached quickly to the glass substrate and the excess OH$^-$ ions attacked the Zn$^{2+}$ ions
decreasing Zn\(^{2+}\) ions that combines to O\(^{2-}\) to form urchin like ZnO structure. When SiO\(_2\) from RHA was added, the silanol and siloxane bridges of SiO\(_2\) attached to the OH\(^-\) ions which competes with Zn(OH)\(_2\), leaving many free Zn\(^{2+}\) ions, thus forming ZnO-SiO\(_2\) with zinc complexes (sulfates and hydroxides of zinc).

Figure 2 shows the morphological structure of ZnO and ZnO-SiO\(_2\) deposited on silicon substrate. It can be observed from Figure 2(a) that a sea-urchin like structure of ZnO was formed far different from the flake-like formation using glass as a substrate. The nanostructures exhibits sharpened tips due to the reactive basic solution resulting to a crystal etching process. The formation of sea-urchin like nanostructures is attributed to substrate used, since silicon has higher surface energy compared to the glass substrate, then nucleation is not fast since high energy is required for the seed nuclei to adhere on the surface. In the process, the Zn(OH)\(_2\) seed nuclei dissociates providing Zn\(^{2+}\) and O\(^{2-}\) that will allow the gradual formation of the sea-urchin like nanostructure. When SiO\(_2\) from RHA was added to the bath solution, hemispherical protruding structures were observed having diameter of about ~4 µm comparable to the diameter of the ZnO sea-urchin like structure. It is possible that the functional groups of SiO\(_2\) from RHA bonded with the OH\(^-\) ions of Zn(OH)\(_2\). As the competition of ZnO and SiO\(_2\) in attracting the OH\(^-\) ions of the Zn(OH)\(_2\) continues, it is possible that more SiO\(_2\) particles are attached to the OH\(^-\) group of the seed nuclei. The extra OH\(^-\) ions in the solution have attached to the SiO\(_2\) particles and will cover the growing sea urchin-like ZnO. The SiO\(_2\) has a lower surface energy than ZnO thus SiO\(_2\) will adhere to the surface on top of ZnO. In these cases, formation of zinc complexes would likely to

Figure 1. Scanning electron micrograph of (a) ZnO and (b) ZnO-SiO\(_2\) deposited on glass substrate.

Figure 2. Scanning electron micrograph of (a) ZnO and (b) ZnO-SiO\(_2\) deposited on silicon substrate.
happen and these may affect the formation of the hemispherical structures. Elemental composition analysis results verified the presence of ZnO and ZnO-SiO₂, however it showed the non-stoichiometric ratio of Zn, O and Si suggesting that Zn-complexes are indeed present in the samples.

Table 1 shows the elemental composition of the grown ZnO and ZnO-SiO₂ nanostructures deposited on glass and silicon substrates. For ZnO deposited on glass, the [Zn] to [O] ratio is not equal to unity. It is believed that the ZnO structures are formed with some zinc complexes such as Zn(HSO₄)₂ and (NH₄)₂ZnO. For ZnO-SiO₂ also on glass, large atom composition of Zn and O atoms were detected. The solution is oxygen rich due to the precursors and the substrate. Silicon atom has significant percentage observed after the incorporation of SiO₂ powder. The ratio of Zn to O is not significant, it decreases with respect to [Zn]/[O] ratio of the bare ZnO, showing high percentage of oxygen atom. The number of oxygen atoms also increases when added with amorphous SiO₂ powder. It further suggests that the formations onto the substrate are not pure ZnO-SiO₂, but there is also zinc complexes incorporated during the formations.

For the ZnO on silicon substrate, the [Zn] to [O] ratio is equivalent to 4.21 depicting that an excess of zinc is present on the grown ZnO nanostructures. For the ZnO-SiO₂ on silicon substrate, the hemispherical structures are composed rarely of Zn with a trace amount of SiO₂ due to SiO₂ powder at the surface which indicates that the SiO₂ are possibly covers the ZnO since large percentage are attributed for Si and O atoms.

Table 1. Quantitative EDS data (% atom) of ZnO and ZnO-SiO₂ nanostructures deposited on glass and silicon substrates

| Element | Glass substrate | Silicon substrate |
|---------|-----------------|-------------------|
|         | ZnO             | ZnO-SiO₂          | ZnO              | ZnO-SiO₂         |
| Zn      | 38.25           | 22.05             | 77.81            | 1.01             |
| O       | 60.20           | 56.35             | 18.48            | 55.83            |
| Si      | 1.55            | 21.60             | 3.71             | 43.16            |

3.2. Infrared Characteristics
The infrared characteristics of ZnO-SiO₂ nanostructures deposited on glass and silicon substrates are shown in Figure 3. The characteristic peaks at 738 cm⁻¹ and 642 cm⁻¹ are observed indicating the presence of ZnO. The peaks at 1042 cm⁻¹, and 830 cm⁻¹ are the characteristic peaks for Si-O-Si asymmetric and symmetric stretching, which indicate the presence of SiO₂ on the sample. The two distinct peaks for Si-O-Si bending at 1502 cm⁻¹ and Si-OH at 1386 cm⁻¹ are attributed to the SiO₂ particles from RHA that attached to ZnO. The characteristic peaks for O-H stretching and bending vibration absorption at 3329 cm⁻¹, 1642 cm⁻¹, and 704 cm⁻¹ are shown also in the FTIR spectra which correspond to the adsorbed water and for the Zn-complexes like zinc hydroxides and zinc sulfates. The presence of numerous O-H vibrations suggests that there is significant volume of Zn-complexes deposited for both substrates. This supports the EDX results that show a ratio of Zn and O which is near to the stoichiometric ratio of Zn to O for Zn(OH)₂.

The absorption peak at 940 cm⁻¹ that corresponds to Si-O-Zn stretching is also observed which confirms that the SiO₂ from RHA has bonded with ZnO nanoparticles. A span of peaks is observable between 2400 cm⁻¹ and 1900 cm⁻¹ and this may be due to the dissolved volatile species like CO₂ which is acquired when exposed to air. The spectrum of ZnO-SiO₂ deposited on glass has more pronounced absorption peaks than the spectrum of the nanostructures deposited on silicon because of the SiO₂ composition of the amorphous glass substrates.
Figure 3. Infrared spectra of ZnO and ZnO-SiO$_2$ deposited on glass and silicon substrates.

4. Conclusions
ZnO-SiO$_2$ nanostructures have been deposited on glass and silicon substrates via chemical bath deposition method. SEM-EDX and FTIR reveals the incorporation of SiO$_2$ on ZnO surface. Flake-like ZnO-SiO$_2$ is deposited on glass substrate while protruding hemispherical structures are deposited on silicon substrate. Flake-like ZnO-SiO$_2$ nanostructures are due to a high nucleation rate and a high growth rate in a high OH$^-$ concentration. Precipitates quickly formed at a high concentration and random sites acted as nucleation sites for the nanostructures. As a result, random growth directions of ZnO-SiO$_2$ causing flake-like structures. The high growth rate does not allow enough time for ions to move into proper sites. The surface morphology and the infrared characteristics of the ZnO-SiO$_2$ nanostructures depend on the concentration and substrate being used. Results also showed that the synthesized nanostructures are not pure ZnO-SiO$_2$ but there are also Zn-complexes incorporated into the formations.

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