Growth of chemically deposited ZnO and ZnO-SiO₂ on Pt buffered Si substrate

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Abstract. Growing ZnO on Si via low-cost CBD is difficult owing to the large lattice mismatch between ZnO and Si and the intricate control of nanoparticle aggregation. In this work, a Pt buffer layer and addition of SiO₂ on the chemical solution were introduced. The effect of these parameters on the resulting morphology and composition were investigated using SEM-EDX and FTIR. Pt-coated Si showed higher density of ZnO nanostructure growth than bare Si due to the additional nucleation sites provided by Pt. Moreover, SiO₂ addition resulted to a different ZnO nanostructure.

1. Introduction
The drive for nanosized semiconductor led to a large number of researches on different semiconductor for various applications. One of the most promising materials available is zinc oxide (ZnO) which has a direct wide bandgap of 3.37 eV, a large exciton binding energy of 60 meV at room temperature and a stable wurtzite structure [1]. Aside from those mentioned, ZnO is easily acquired and is a relatively low cost material making it a popular choice as semiconductor. Also, it can be grown on various substrates using chemical bath deposition (CBD), a low cost simple deposition method for synthesizing a wide variety of ZnO nanostructures [2]. But some substrates such as the extensively used sapphire are very expensive and are electrically insulating materials that introduce difficulty in device fabrication. Alternatively, silicon (Si) substrates have higher carrier mobility and can be easily integrated with on-chip circuitry and Si-based devices. However, the growth of ZnO is particularly challenging due to the large lattice mismatch between ZnO and Si.

This problem can be solved by the introduction of a buffer layer to facilitate ZnO growth. Platinum (Pt) is a good candidate due to its smaller ZnO plane misfit [3]. In addition, there is a tendency of ZnO to adsorb strongly on the noble metals such as Pt since they are known to be good catalyst for deposition. Also, Pt displayed good stability under harsh conditions due to its resistance to oxidation [4] and Pt-coating on substrates showed enhancement of electrical contact during growth. Though there is inadequate works done focusing on its effect, it is believed that the metal coating of the substrate has an influence on the morphology, size and shape of ZnO [5]. In spite of this, ZnO

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synthesis in the desired dimension specifically as nanosized structure has limitations due to difficulties in controlling the nanoparticle aggregation [6].

Researches focusing on the surface modification of ZnO found out that the addition of surface cappers such as the chemically stable silica (SiO₂) will inhibit particle growth and aggregation [7] leading to better control on the shape and size of the ZnO structures in the particle growth solutions resulting to higher surface to volume ratio. Furthermore, the addition of SiO₂ which acts as an embedding matrix modifies defect structures and transition mechanisms [8]. But most studies done concerning silica-added ZnO (ZnO-SiO₂) are synthesized using sol-gel technique that yielded powders instead of depositing these nanostructures on substrates.

Despite it being a fascinating area of research, there are limited amount of literature available that tackles it. This problem leaves a dent in research advancement such as the morphology, growth behaviour and unique properties of ZnO-SiO₂ deposited on commonly used Si substrates which could possibly lead to interesting discoveries. This study therefore examines the effect of Pt buffer layer to the growth of chemically deposited ZnO and ZnO-SiO₂ by comparing their growths on bare and Pt-coated Si substrate. This paper would also explore the possibility of enhancing the ZnO structures grown on Si by the addition of silica powders. The resulting morphology and composition were examined.

2. Experimental details

In this work, ZnO and ZnO-SiO₂ nanostructures were both synthesized using ammonium zincate solutions from 0.03M zinc sulphate and 1.0M ammonium hydroxide. The solutions were stirred at 360 rpm for thirty minutes to allow proper mixing of the precursors. But in preparing ZnO-SiO₂, silica was added after mixing the precursors. Both solutions were then immersed in a water bath and heated to 70°C while stirring them at 360 rpm. Pre-cleaned silicon (Si) substrates, with and without Pt-coating, were then immersed in the solution baths for five hours allowing ZnO and ZnO-SiO₂ nanostructures to deposit on the substrates. The substrates were then taken out of the bath and rinsed with distilled water preheated to 70°C to remove loosely adhering particles. The fabricated samples were scanned using JEOL JSM-6510LA Analytical Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) employing 20kV accelerating voltage to obtain micrographs of the morphology of the deposited structure and its composition. Also, the samples were scanned in the range of 650-4000cm⁻¹ via Perkin Elmer Spectrum 100 FT-IR spectrometer to identify the functional groups present.

3. Results and Discussions

SEM micrographs of ZnO deposited on bare and Pt-coated Si substrates are obtained and displayed in Figure 1. Figure 1(a) reveals that there are very few structures grown directly on the substrate. A larger magnification, shown as Figure 1(b), indicates that these round structures are urchin-like clusters made up of radially adhering hexagonal nanorods with flat tips averaging at 478 nm wide. EDS data of these structures, listed in Table 1, indicate very high Zn and O content which confirms that these are actually ZnO structures. Figure 1(c), on the other hand, shows that the Pt-coated Si surface have numerous grown structures. It is obvious that this surface has higher growth density of structures as compared to the bare Si substrate. Greater magnification, shown as Figure 1(d), reveals that clusters of flat-tipped hexagonal nanorods are grown on the surface. Growth aggregation can also be observed as thinner rods grow along the structure of thicker rods. These thinner rods having an average diameter of 122 nm accumulate in the spacings between thicker rods having an average diameter of 325 nm. Both the thin and thick rod structures are believed to be ZnO as indicated by their EDS data.

These results show that ZnO deposited on bare Si have lower growth density of structures compared to those deposited on Pt-coated substrate. The ZnO growth density difference between these substrates can be attributed to the larger lattice mismatch on ZnO-Si than on Pt-coated ZnO. This eventually led to the difficulty in growing ZnO on bare Si and also explains the higher growth density.
on Pt-coated Si substrate. Aside from that, the presence of Pt makes ZnO easier to nucleate. The Pt layer had acted as a nucleant layer promoting the growth of additional nucleation sites for ZnO to adhere. This is also supported by a more stoichiometric [Zn]/[O] ratio of 1.75 for Pt-coated Si compared to 2.24 ratio for bare Si. In addition, during the deposition of ZnO, a secondary growth of ZnO was observed. The cluster of thicker nanorods of ZnO served as spherical seed for the growth of thinner ZnO nanorods which were preferentially formed on these clusters. These primary clusters served as building blocks for the dense growth of more ZnO nanorods.

**Table 1.** EDS data of ZnO deposited on bare and Pt-coated Si substrate.

| Substrate          | %O  | %Zn | [Zn]/[O] |
|--------------------|-----|-----|----------|
| bare Si            | 30.86 | 69.14 | 2.24     |
| Pt-coated Si       | 36.38 | 63.62 | 1.75     |

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thinner ZnO nanorods which were preferentially formed on these clusters. These primary clusters served as building blocks for the dense growth of more ZnO nanorods.

In contrast, ZnO-SiO$_2$ deposited on bare Si, shown in Figure 2(a), exhibited a fibrous-like layer with cracks that evenly covered the whole substrate. A larger magnification, shown in Figure 2(b), revealed that the layer wrapping the surface has very high Si content. On the other hand, ZnO-SiO$_2$ deposited on Pt-coated silicon, shown in Figure 2(c), had formed structures on the Si surface. The surface has low density of growth but is better compared to bare Si which showed no rod-like structure at all. A higher magnification, indicated as Figure 2(d), shows that these structures are clustered together and appeared to form flower-like structures. These structures have radially adhering rods that narrows towards its tips. These rods are not smooth but are irregularly shaped. Its EDS data, also, revealed very high Zn content. These results further support the belief stated earlier about the role of Pt on the growth. The presence of Pt layer provided nucleation sites that promote the growth of ZnO structures on the surface.

Table 2. EDS data of ZnO-SiO$_2$ deposited on bare and Pt-coated Si substrate.

| Substrate   | %Si   | %O    | %Zn  | [Zn]/[O] |
|-------------|-------|-------|------|----------|
| bare Si     | 50.11 | 39.89 | 10.00| 0.25     |
| Pt-coated Si| 10.58 | 18.91 | 70.51| 3.73     |

Figure 2. SEM micrographs of ZnO deposited on (a) bare and (b) Pt-coated Si substrates and ZnO-SiO$_2$ deposited on (c) bare and (d) Pt-coated Si substrates.

Comparison of Figures 1 and 2 gives insight to the effect of SiO$_2$ addition to the structure. Without adding SiO$_2$, the structures formed were urchin-like clusters made up of hexagonal rods with flat tips. However, the addition of SiO$_2$ has significantly changed the morphology on the surface. For bare Si, a SiO$_2$ layer was observed while for Pt-coated Si, a flower-like structure with less aggregation was
perceived. This morphological modification was clearly due to the addition of SiO₂ into ZnO. Since SiO₂ is a nonpolar network, it attaches itself to the non-polar facets of ZnO and leaves the polar face exposed for crystal growth. That attachment to the non-polar sides inhibits the would-be-hexagonal structure into something different such as that seen in Figure 2(d). The adherence of SiO₂ on the non-polar sides leaves ZnO growth only to its polar facets thus significantly decreasing the aggregation of structures.

The bonding interactions are also investigated using FTIR spectroscopy with results shown in Figure 3. The peaks detected in 706-789 cm⁻¹ range is due to Zn-O bonding. These peaks are visible to all samples indicating the presence of ZnO deposition for all samples. Also, the points in the range of 3220-3240 cm⁻¹, 1391-1508 cm⁻¹ and 1030-1090 cm⁻¹ are attributed to Si-OH vibrations, Si-O-Si bending and Si-O-Si stretching vibrational modes, respectively. These peaks are present to ZnO on bare Si and to ZnO-SiO₂ on both substrates and are absent to ZnO on Pt-coated substrate further supporting the SEM-EDX results. ZnO was directly deposited on bare Si thus Si-O bonds are expected unlike ZnO deposited on Pt-coated Si where Si-O bonds are deficient due to the presence of Pt between ZnO and the Si substrate. This result implies that the Pt acted as a buffer that discouraged Zn or O interaction to Si substrate.

![FTIR spectrum](image)

Figure 3. FTIR spectrum of ZnO on bare Si (black line) and Pt-coated Si substrates (green line) and ZnO-SiO₂ on bare Si (red line) and Pt-coated Si substrates (blue line).

The same can be said with ZnO-SiO₂ on bare Si, however the addition of SiO₂ means that there will be more Si-O bonds than on bare Si which is obvious with its FTIR spectrum (red line) results. This further suggests that the layer seen on Figure 2(a) and 2(b) is composed mainly by SiO₂ as verified by its EDS data. Also, ZnO-SiO₂ on Pt-coated Si still registered Si-O bonds due to the addition of SiO₂ thus validating the absorption peaks observed in its FTIR spectra (blue line). Since Pt-coated the substrate, Si-O bonds detected in its IR spectra suggests that SiO₂ may have adhered with the non-polar sides of the grown ZnO nanostructure. This results to a different nanostructure and the reason why hexagonal rods are not detected in its morphology.

4. Conclusion
ZnO and ZnO-SiO₂ were grown on bare and Pt-coated Si substrates. Few hexagonal ZnO nanostructures adhered to bare Si while numerous hexagonal ZnO nanostructures grow on Pt-coated Si substrate. The catalytic Pt buffer layer promotes growth of ZnO by providing additional nucleation sites on the surface. In contrast, ZnO-SiO₂ deposited on bare Si revealed only a porous layer with the absence of any ZnO structure however ZnO-SiO₂ grown on Pt-coated Si showed low density of irregularly shaped rods. The adhesion of SiO₂ network discourages the formation of ZnO hexagonal
structures. This result is further supported by the FT-IR where numerous Si-O-Si functional groups were detected particularly to SiO₂ added ZnO samples.

5. References

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