The effect of surface morphology in copper oxide nanostructure to photo detector characteristics

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Abstract. We study the effect of structural properties of copper oxide nanostructure and its sensitivity for photo detector application. Copper oxide (CuO) nanostructures were prepared by combining the thermal evaporation with dry oxidation. We select CuO system at different thickness (around 90, 170, and 270 nm) and X-ray diffraction spectra confirms their polycrystalline structure. Scanning electron microscope images show the distinct CuO morphology surface for each sample on which the grain shape is changed and the size is grown with the increasing of the CuO thickness. Fourier-transform infra-red spectra reveals the high penetration depth of oxygen at ~90 nm thick sample indicated by large Si-O-Si bond intensity. Photo current characterization for each sample is carried out to compare its light sensing properties. We found that the thickness of CuO nanostructure system is related to the sensitivity of device during the light exposure in which thinner samples have better performance. Furthermore different band gap for each CuO sample is predicted from its sensitivity at continuous light exposure. We suggest that the grain boundary and the distinct morphology might promote a unique confined nanostructure effect, resulting in band gap widening. These studies demonstrate a new approach for tunable photonic device efficiency that could be beneficial in reducing energy loss during energy conversion.

1. Introduction

Computer has modernized every single aspect of people life, ranging from factory control to sophisticated scientific machinery. It is based on semiconductor material such as Silicon and Germanium which employ electron movement to carry and process information. Transistor which facilitates such control is characterized by its thickness; overly thick of the chip would not perform well while too thin chip might experience quantum tunneling that causes current leakage. The alternative solution is to combine with photonic technology that uses light as information carrier [1]. Such advancement can be achieved with development of Photo detector that works at low energy with minimum loss and detects wide range of photon wavelength. Alteration of certain aspect in material can be done to manage the requirement, and in this case is nanostructure [2]. Engineered diminutive structure of material can substantially change the electronic structure of material with an effect called Quantum confinement. With tunable electronic energy level, we can produce photo detecting device to suit our needs to detecting light property.

In this paper, we investigate the properties of copper oxide (CuO) light sensor with distinctive surface morphology. CuO nanostructures are fabricated by simple method of metallization and oxidation, and variations of surface are obtained through thickness difference. White light from LED...
that contains different wavelengths will be used as light source. X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectra will be used to determine the differences in crystal orientation and atomic bonding at each nanostructure. Scanning Electron Microscope (SEM) is used to verify the nanostructure visually. Finally, photo current characterization of nanostructure was performed to analyze its sensing characteristic, and then a model derived from Brus equation is used to explain this phenomena [3].

2. Experimental Method

Device has been developed by using simple method of thermal annealing, metallization and dry oxidation. In the beginning stage, a thin layer of copper is deposited on RCA pre-cleaned silicon substrate. We use 99.999% pure copper wire to grow such layer and vary its length into 2 mm, 3 mm, and 4 mm in order to fabricate the samples with 3 different thicknesses. Then, these samples were oxidized in rich oxygen environment at atmospheric ambience (600°C for 4 hours). Finally, metal contacts were prepared at the sides of each sample. Each sample was characterized with X-Ray diffraction spectra, Fourier transform infra-red spectra, Scanning electron microscope and photo current characterization.

3. Result and Discussion

In order to find the thickness of our structure, we used Spectroscopic Ellipsometry (SE) equipment in the energy ranges of 1.2 to 6.5 eV. For Cu films, Lorentz model was used in the fitting process ranging in the full energy spectrum of SE data and we found that the thickness of Cu films are 50 nm, 59 nm and 62 nm from 2 mm, 3 mm and 4 mm of length of copper wire respectively. In the fitting and analysis of CuO structure from SE data, Cauchy model that describes transparent material was used in energy ranges below energy bandgap (transparent area) for obtaining the thickness of CuO that are 90, 170 and 270 nm respectively.

Figure 1. (a) SEM imaging shows surface structure of Copper Oxide with 90 nm thickness, fine grain structure is observed; (b) the surface of 170 nm thick CuO indicates dotted structure with diameter ranging from 117 to 150; (c) surface of the 270 nm thick CuO is flat with boundary of the grain even smaller, ranging from 59 to 100 nm.
Figure 1 shows visual morphology of CuO nanostructure with different thickness obtained by SEM imaging. Figure 1(a) depicts the surface of 90 nm thick sample which shows fine grain of CuO cluster that spread almost evenly. This image shows that there is no gap between each cluster and suggests that every single cluster is connected each other to form a CuO layer. Figure 1(b) shows the surface morphology of the sample with the thickness of 170 nm. Dark background and some white dots indicated a tiny cluster of CuO with diameter of approximately 117 to 150 nm is sitting on the top of CuO layer, and these tiny dots are small enough to quantum confinement effect to take place. Figure 1(c) is the surface of 270 nm CuO sample. Noting the relatively same coloration of image and small crack with distinct black color that separates the layer into cluster, there is a strong indication that small flat fraction of CuO layer has been formed with diameter of 58 nm to 100 nm. As these fractions are even smaller than the dots before, we can also expect that the confinement effect to be occurred.

Figure 2 shows XRD spectra of all CuO nanostructures. In general, all of the CuO samples have a good crystalline structure which is indicated with some sharp peaks at common points that correspond with crystal orientation of (111), (-111), and (-113) respectively [4]. However, some of the structure developed a unique orientation correlated to the thickness. At CuO sample with the thickness of 170, the new peaks emerge at points correlated with (110) orientation, meanwhile in the thicker sample of 270 nm, an additional new peaks indicated crystal with (-311) direction is found [4,5]. Comparing the intensity of spectra at these points in each sample, we can conclude that as the thickness increase, CuO structure forms a better crystal and promotes more diverse crystal orientation.

Figure 3 shows FTIR spectra of the CuO nanostructure systems, confirming several important bonding such as Cu-O, Si-Si, and Si-O-Si [6,7]. The copper and oxygen bonding are observed in all samples with distinction in absorbance intensity which depends on the thickness of each sample. At the thinner CuO sample, the FTIR spectra reveals that Si-O-Si bond was formed and shows the highest absorbance intensity compared to the thicker layer, which it indicates the decreasing quantity of this bond that is directly related with increasing copper oxide layer. These results confirm the oxygen penetration through the copper layer that easily bonds with Silicon substrate at relatively thin layer.

**Figure 2.** XRD spectra of all samples indicate all crystal orientation formed and crystalline of each.

**Figure 3.** FTIR spectra show important atomic bonding between Oxygen, Copper, and Silicon.
Figure 4. Figure (a) shows experimental setup for Photo current characterization and the current respond when no photon introduced in the system, notable feature is not observed, which is contrary with figure (b) that shows noticeable increment in current characteristics; figure (c) shows photo current character when photon only given when voltage have integer value; figure (d) shows IV characteristics when light stimulates sensor at certain interval in respect with voltage, in this case only at 1 to 2 volt and 3 to 4 volt the light switched on.

Using the experimental setup as shown above, the photo current relation is investigated. We measure the photo current characteristics at the maximum exposure of halogen light source that used measurement configuration. Figure 4(a) and (b) show the Photo current performance of the device. At the absence of light stimuli, electron current in sensors do not increase much even when the applied voltage is increased, in contrast, noticeable increment is observed when exposure is given, clearly photon energy given has interacted each unique nanostructure and yield different electron current properties. Since the voltage and light source is identical, there is a strong indication that these results are triggered by the structure of each nanostructure.

These experiments reveal a unique pattern which extrapolates from all of sensors, the electron current seems increasing in respect with voltage and increases rapidly after exceeding the current boundary value of $2.0 \times 10^{-4}$ Ampere. The applied voltage where this phenomenon occurs also vary in increasing fashion as the sample getting thicker, and it means the energy used by electron to cross band gap of device to achieve the current boundary value is increasing. It also means that nanostructure developed alters the electronic structure therefore resulting in I-V shifting. SEM image analysis confirms structural differences between samples. As the confinement radius of structures is
smaller, the band gap structure of material is expected to change as governed in Brus equation (equation 1).

$$\Delta E = E_{qd} - E_{bulk} = \frac{\pi^2 \hbar^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon_0 \varepsilon_R R}$$  

Where $E_{qd}$ is band gap energy for confined material, $E_{bulk}$ is band gap energy for bulk material (in CuO 1.6 eV [8]), $m_e$ and $m_h$ are respectively electron effective mass and hole with value of 0.4 $m_o$ [9] and 9.7 $m_o$ [10] ($m_o$ is electron rest mass), $\varepsilon_r$ is dielectric constant ($10^4$ for CuO [8]) and $R$ is nanodot radius. Using this and radius information, calculated band structure widening is shown at table 1. The results conclusively explain the band gap alteration due to different confinement size which leads to phenomenon above. Besides the confinement effect, crystal orientation taking major role explaining the band gap difference, as mentioned before as Copper Oxide thicker, it is more diversified and will lead to a lot of lattice mismatch that interfaces different crystal orientation [11]. Space between Copper and Oxygen atoms would slightly move and change band structure entirely ranging from band gap widening to redirect valence state into another crystal point which means extra energy needed to excite electron [12,13].

| Nanostructure Diameter | Band Gap Widening | Wavelength equivalent |
|------------------------|-------------------|-----------------------|
| 58 nm                  | 0.001 eV          | 824.6 nm              |
| 117 nm                 | 0.00026 eV        | 825 nm                |

In the next part, we evaluate the response and sensitivity of Copper Oxide sensor by exposing the system with light stimuli at the intermittent mode. Figure 4(c) depicts the I-V properties that indicate current response to exposure. Copper Oxide sample with 90 nm thickness shows the high sensitivity, while the sensitivity decrease when CuO thickness increases. So in this study, CuO sensor with 270 nm thick Copper Oxide layer has the least sensitivity. In addition, figure 4(d) shows I-V response when light is applied at certain voltage interval. It shows the rapid changes and is interpreted as the effect of the light switching.

4. Conclusion
Nanostructured Copper Oxide photo detector has been developed successfully by varying the CuO layer thickness. Distinct surface structure has been confirmed by SEM image and leads to the structure that could introduce the confinement effect. From the structural point of view, our results show that thicker CuO layer promotes the good crystallinity with more crystal orientation. It is important to conclude that photo current characterization shows the different response as the effect of carrier confinement on the surface and also due to the distinct crystallinity. This research demonstrated the controlling of photo detector characteristics by surface morphology modification.

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