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## Size Dependent Gold Assisted ZnO Growth on Si Surface by Continuous Spray Pyrolysis Reactor for Light Suppression

Hrishikesh Dhasmana<sup>a,b</sup>, Charu Dwivedi<sup>a</sup>, V Dutta<sup>a,\*</sup><sup>a</sup> Photovoltaic Laboratory, Centre for Energy studies,  
Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India<sup>b</sup> Department of Applied Science, Echelon Institute of Technology, Faridabad-121101, India

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### Abstract

Colloidal Au particles of sizes 15 and 40 nm are spray deposited on polished Si surface and then the deposition of ZnO nanostructure layer using Continuous Spray Pyrolysis reactor is performed. XRD data suggests that the larger size Au nanoparticles act as seed particles for ZnO nanostructure formation, while smaller Au nanoparticles favour (002) oriented growth. SEM measurement confirms enhancement of ZnO nanorods growth in the case of 40 nm Au assisted deposition. The reflection measurement shows higher surface plasmon resonance for larger size Au particles and hence significant light reduction up to 51% of existing value in 500-900 nm wavelength region is achieved which may ultimately help in the increase of photocurrent in Si solar cells.

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\*Corresponding author. Tel.: +91-11-26591261; fax: +91-11-26591261.

E-mail address: [vdutta@ces.iitd.ac.in](mailto:vdutta@ces.iitd.ac.in).

## 1. Introduction

In a crystalline Si solar cell, the efficiency of the device can be increased by optical coupling of the light incident on Si surface. The optical reflection losses from the surface are very critical in determining the ultimate efficiency of Si solar cell and account for ~5% efficiency reduction [1]. The surface texturisation and antireflection coating help in reducing the reflection loss [2]. A 42.7% reduction of reflected light can result in the enhancement of Si solar cell efficiency by 112.4% [3].

The light suppression by nanostructure layers has gained popularity for devices like silicon solar cells and can enhance efficiency by the way of increasing photocurrent. Surface Plasmonic effects using Au and Ag nanoparticles (NPs) have also given rise to improved performance. Since ZnO nanostructures can be formed on Si using a seed layer, Au NPs as seed layer can assist the ZnO nanostructure growth as well as give rise to the surface plasmonic effects. The phenomenon of Localised Surface Plasmon Resonance (LSPR) can occur and help improve the solar cell performance [4, 5]. The resonance wavelength depends on the nanoparticle's size, shape, and local dielectric environment [6, 7].

Zinc oxide (ZnO) has inherent material properties such as good transparency in visible wavelength region, appropriate refractive index (nearly 2), ability to form textured coating via anisotropic growth, good chemical stability etc. Therefore, ZnO can play a useful role in Si solar cell as an antireflection layer [8, 9]. ZnO nanostructure such as porous particles is also reported for minimising reflection loss [10]. The growth of controllable ZnO nanostructure on Si surface can be achieved by gas phase synthesis method [11, 12]. But technological incorporation of these methods in existing Si solar cell fabrication technology may be difficult. Therefore, a simple inline process to create ZnO nanostructures on Si surface will be useful.

The continuous spray pyrolysis (CoSP) reactor includes all the features required for this purpose and has been established in the lab for fabricating NPs as well as nanostructure layers on glass [13]. The addition of Au NPs in ZnO nanostructure growth has been studied by various research groups and is suggested for its role as a seed layer and catalytic layer in the ZnO growth [14-17]. The paper reports on the growth of Au assisted ZnO nanostructure layer on Si surface and the reflection study suggests a better light coupling does become possible.

## 2. Experimental section

The experimental set up of CoSP reactor for the growth of ZnO nanostructure is explained in a recently reported work [18]. The experimental procedure followed for ZnO growth on various Si substrates by CoSP reactor is explained in Fig. 1. The sample details for various ZnO nanostructures on polished Si surface by CoSP reactor are given in the Table 1.

The crystal structure and surface morphology of ZnO nanostructures over (100) Si surface were investigated by Philips XPERT PRO (PW3040) X-Ray Diffractometer (XRD) and ZEISS EVO-50 model Scanning Electron Microscope (SEM). Optical reflectance spectra in the wavelength region 300-1200 nm were obtained using Perkin-Elmer Lambda-1050 UV-VIS-NIR spectrophotometer.

Table 1. Table for ZnO nanostructure on polished Si surface

Sample details	Sample name
ZnO growth on Si surface with Zn solution seed layer only	SP
ZnO growth on Si surface with Zn solution seed layer assisted by 15 nm Au particles	Au_15
ZnO growth on Si surface with Zn solution seed layer assisted by 40 nm Au particles	Au_40
ZnO growth on Si surface with Zn solution seed layer assisted by 1.3 nm thin Au film	Au_1.3
ZnO growth on Si surface with Zn solution seed layer assisted by 1.3 nm thin Au film and annealed at 350°C temperature for 30 minutes	Au_1.3_350
Bare polished Si surface	Si surface
Only 1.3 nm thin Au film on Si surface	Au/Si
Only spray deposited 40 nm Au particles on Si surface	40 nm Au NPs/Si
Only spray deposited 15 nm Au particles on Si surface	15 nm Au NPs/Si

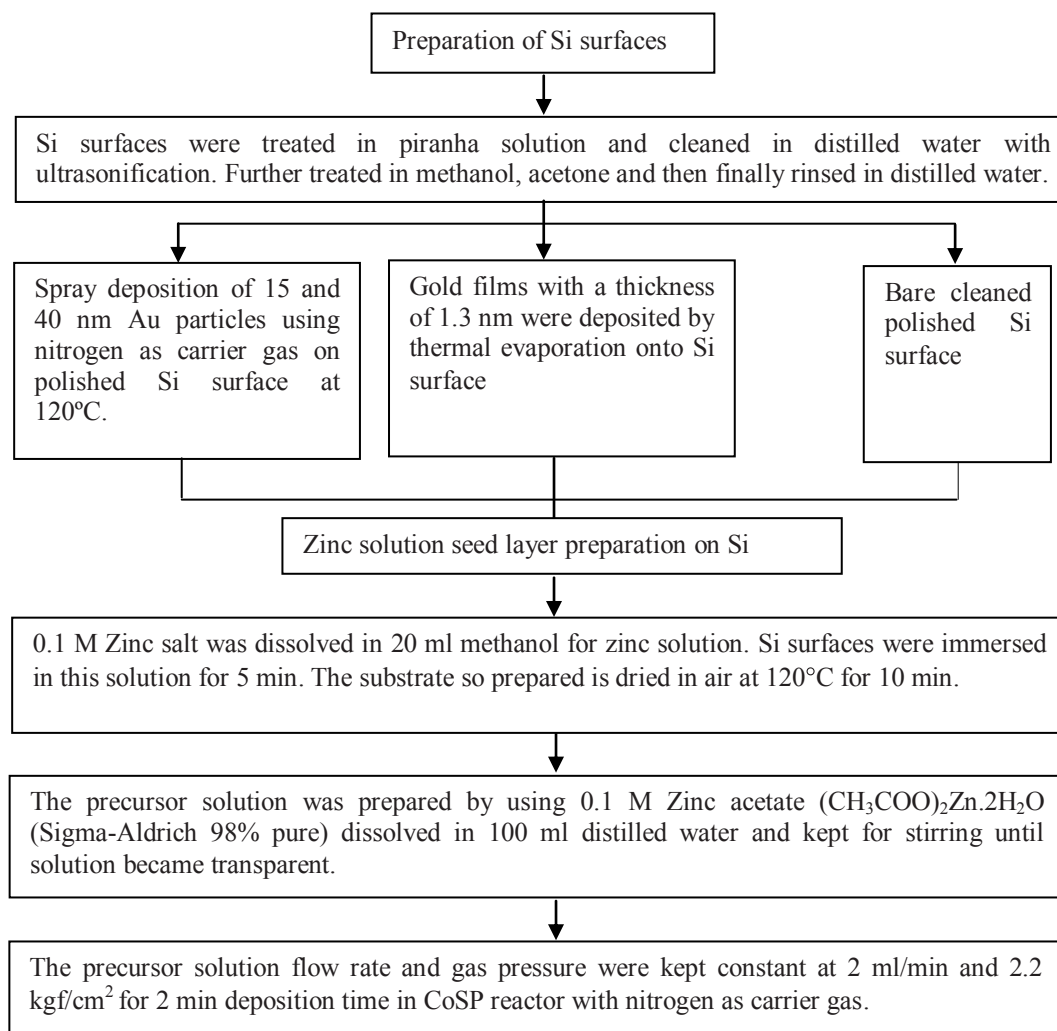


Fig. 1. Flow chart of experimental procedure for ZnO nanostructure by CoSP reactor

### 3. Results and discussion

#### 3.1. Structural analysis

Figure 2 shows indexed XRD pattern (JCPDS, File No. 36-1451) of ZnO nanostructure layers for 3 samples SP, Au\_15 and Au\_40. In the case of Au\_15, (002) oriented ZnO growth is observed (Fig. 2 (b)). The role of Au NPs layer for ZnO growth is changed in the case of Au\_40 and this is confirmed by the presence of matching corresponding extra Au fcc peaks (JCPDS, File No. 4-0784)(Fig. 2(c)).

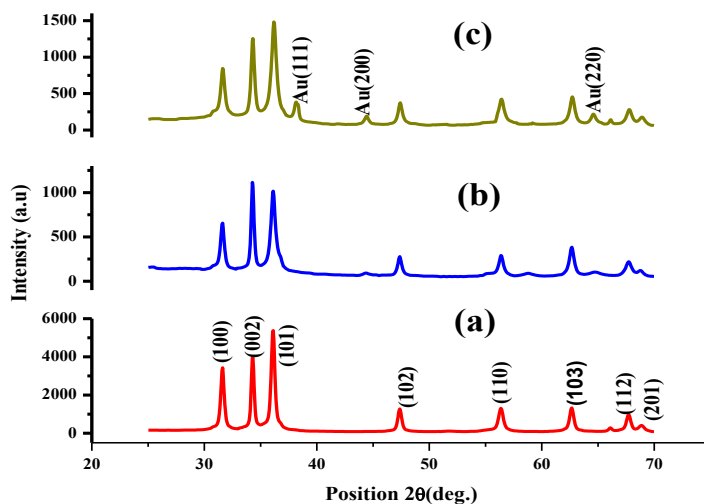


Fig. 2. XRD spectra for (a) SP (b) Au\_15 (c) Au\_40

#### 3.2. Surface study

Surface morphology of ZnO growth on top of Zn solution seed layer assisted by 1.3 nm thin Au film is shown in Fig. 3(a). A portion of Si surface consists of continuous ZnO film growth with flakes of Au film is shown as an inset image. Figure 3(b) shows the formation of multibranched nanorods on Si surface for SP. Zinc (Zn) solution seed layer promotes nanorod growth, but it does not lead to vertically aligned nanorods, may be because of low deposition time. Si surface area coverage is also an issue with this type of growth. These shapes of nanorods are irregular and a large size variation among nanorods is observed. But if the ZnO deposition is done on different sizes of Au particles such as 15 nm and 40 nm along with Zn solution seed layer, the ZnO film growth profile is changed for the same deposition condition of CoSP reactor. In the case of ZnO growth for Au\_15, coalescence amongst nanorods starts (the inset image of Fig. 3(c)) and increased surface area coverage is also seen. This changed growth profile may be attributed to changed roughness profile due to the presence of Au NPs. Figure 3(d) shows different ZnO growth for Au\_40. In this case, an active participation of Au NPs as seed layer in ZnO growth increases Si surface area coverage and also the coalescence amongst nanorods. More uniform ZnO nanorods of sizes ~150 nm are observed. Elemental presence in gold assisted ZnO growth for Au\_40 is further confirmed with the help of Energy Dispersive Analysis by X-Ray (EDAX) measurements shown as an inset image.

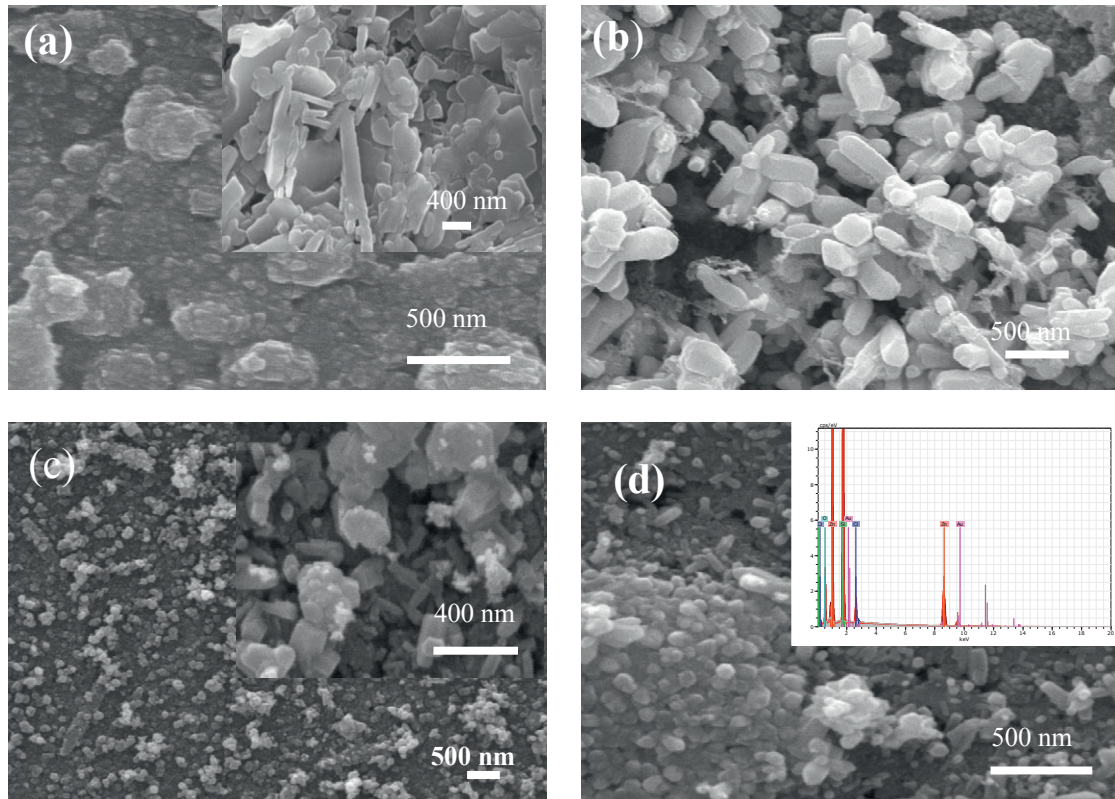


Fig.3. SEM measurement for (a) Au\_1.3 (b)SP (c) Au\_15 (d) Au\_40

### 3.3. Reflection measurement

Reflection measurement for polished Si surface, Au thin film, Au NPs layer and gold assisted ZnO growth on Si surfaces is shown in Fig. 4. Figure 4(a) shows highly reflecting gold film on Si surface. On comparing light reflection of gold thin film and Au NPs on Si surface with polished Si surface, relatively higher absorption is observed  $\sim 500$  nm wavelength region (Fig. 4(a) and Fig.4(b)). This fall may be attributed to localised surface plasmon resonance phenomenon. After ZnO growth on Au thin film, the light reflection appreciably goes down to nearly 15 % from 65% in the wavelength region 500-1200 nm. On further annealing this film at 350°C for 30 minutes, slight low reflection is observed for Au thin film (Fig. 4(a)). Figure 4(b) shows the reflection from various size gold particles film on Si surface by spray deposition. This reflection spectrum clearly confirms that a higher absorption is observed for the case of 40 nm Au particles on Si surface. Figure 4(c) shows the reflection measurement for polished Si, SP, Au\_15 and Au\_40 surfaces. The constant absorption edge for ZnO is clearly visible in the reflection spectrum for all the ZnO films. The multibranch ZnO nanorod surface morphology for SP does not change reflection appreciably on Si surface. But in the case of gold assisted ZnO thin film growth, reflected light reduction is appreciable. The average reflection value in 500 – 900 nm wavelength regions for Si surface, SP, Au\_15 and Au\_40 are 38.5%, 35.4%, 20.6%, 18.7% respectively. The average reflection value for Au\_40 is reduced to 37.8% as compared to 44.1 % for Au\_15 in wavelength region 450-650

nm, which is almost 15% fall of R value for the case of Au\_40. Thus, there is a reduction of nearly 51% of R value for Au\_40 in 500-900 nm wavelength regions, which can be attributed to the combination of ZnO nanostructure formation and LSPR.

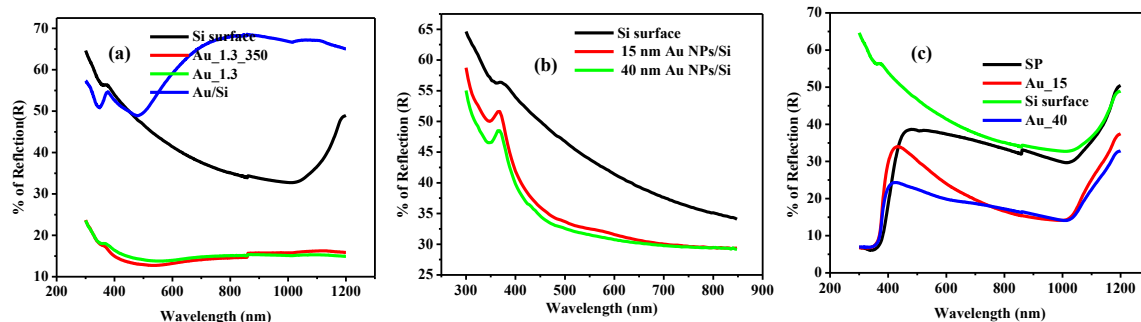


Fig. 4. Reflection measurement for (a) 1.3 nm thin Au films on Si (b) Au NPs on Si (c) SP, Au\_15 and Au\_40

#### 4. Conclusion

This work shows the effect of the growth of gold assisted ZnO nanostructure layer on Si surface by CoSP reactor for optical enhancement. XRD measurement confirms no Au role in ZnO growth for the case of Au\_15, while extra Au fcc peaks are observed for Au\_40. For Au\_40, SEM measurement suggests an increased coalescence amongst nanorods which leads to enhance nanostructure density with more uniformity in the sizes of ZnO nanorods. Reflection measurements confirm noticeable 51% and 46.5% of R value fall in 500-900 nm wavelength regions for Au\_40 and Au\_15. The coalescence amongst nanorods, Si surface area coverage and LSPR effect are increased with the sizes of Au particles. The growth of nanostructure layer comprising ZnO nanorods and Au NPs can be achieved in an inline mode by incorporating the CoSP reactor in the existing Si solar cell fabrication line. The ZnO nanostructure layers can be further tuned for the increase in photocurrent and photoabsorption of Si solar cell by changing parameters such as size, density of Au particles under various deposition parameters of the CoSP reactor.

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