Role of Plasmons in Improved Photovoltaic Devices: Nano Clusters of Sn and SnO\textsubscript{x} in SnO\textsubscript{2} Films

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Abstract: Recently, plasmonic concepts have been used to increase absorption length of incident light and separation of excess carriers in photovoltaic devices. Doped SnO\textsubscript{2} films are used as transparent conducting oxide (TCO) in photovoltaic devices. Sputter etched surfaces of SnO\textsubscript{2} films have nano clusters of Sn and SnO\textsubscript{x}. Valence bulk plasmons (VBPs) of nano clusters have been studied using ultraviolet photoelectron spectroscopy (UPS) in in-situ conditions. Transmission and atomic force microscopy (AFM) are used in ex-situ conditions to study surface morphology and optical properties of sputtered SnO\textsubscript{2} thin films.

1. Introduction
Applications of photovoltaic devices for various uses are increasing as cost of production is decreasing. For strategic applications, such as in space and defense, higher efficiency ($\eta$) is more important than cost of solar cells (SCs). On the other hand for mass consumptions, low cost and high $\eta$ are required. Use of concepts of plasmonics to improve $\eta$ of SCs is an active research topic of last decade and presently many groups are active in this field. Review and research articles are available on the use of plasmonics to increase $\eta$ of SCs [1-6]. Maximum $\eta$ of about 30% have been reported of SCs based three junctions of III-V and II-VI semiconductors [7-9]. Maximum $\eta$ of single crystal Si SCs is about 27%, of polycrystalline Si SCs is about 20% and of thin film SCs is about 15% [9]. Maximum $\eta$ of SCs based on polymer semiconductors is about 5% [9]. These maximum $\eta$ are without incorporating concepts of plasmonics. Role of plasmonics is more important in increasing $\eta$ of low cost thin film SCs [2,3,10].

Books and review articles related to bulk and surface plasmons and their applications in various fields are available [11-12]. There is little confusion about bulk plasmons in metals, semiconductors and insulators. The free carrier density in semiconductors is much less than in metals and it is zero in insulators at room temperature (=300K), then expected question is that what is the origin of bulk plasmons in insulators? For example, bulk plasmons energy of Au, Al (metals), Si (semiconductor) and SiO\textsubscript{2} (insulator) are 9.1eV, 15.3eV, 16.5eV and 24eV respectively [11, 13]. In metals, intraband transitions of electrons generate bulk plasmons (transitions within a band having the Fermi level). In semiconductors and insulators, interband transitions of electrons generate bulk plasmons (transitions between bands). In metals, free electrons can move through all the bands. In semiconductors, the conduction band is partially filled and the valence band is empty, therefore electrons move between conduction and valence bands, which generates interband plasmons. In insulators, the valence and conduction band are separated by a gap, so the generation of bulk plasmons is possible only between these bands (valence band to conduction band).
valence bulk plasmons (VBPs). Further, let us denote bulk plasmons of metals as free-carriers bulk plasmons (FBPs) to differentiate these with respect to VBPs of semiconductors and insulators. Free carrier density in F doped SnO₂ transparent conducting oxide (TCO) is about 9x10²⁰ cm⁻³ and corresponding energy of FBPs is about 0.43 eV. In comparison, energy of VBPs in SnO₂ is about 18 eV as reported in literature [15, 16]. The energy of FBPs in metallic Sn is about 14 eV [16,17]. Causes of energies of FBPs and VBPs in SnO₂ are good examples to differentiate between bulk plasmons due to free electrons and valence electrons in semiconductors and insulators.

TCO is part of many opto-electronic devices. These are used in large area panels of SCs. Schemes had been proposed to increase the effective absorption length near the band gap energy and in the sub band gap region using concepts of plasmonics [1-6]. Many research groups are working to increase \( \eta \) of SCs, without increasing cost of SCs. It is required to investigate low cost processing steps, which can use benefits of plasmonics, to enhance \( \eta \) of SCs. It had been observed that sputtering creates nano metallic clusters due to difference in the sputtering rates of different constituent elements of semiconductors and TCOs. For example, In clusters in InP, Ga clusters in GaAs, Sn clusters in SnO₂ etc. had been observed on sputtered surfaces [18-20]. Many groups had used nano clusters of costly metals such as Au and Ag, to increase \( \eta \) of SCs by incorporating concepts of plasmonics [1-6]. One can use nano clusters produced during sputtering of semiconductors and TCOs in geometries of SCs, in place of nano clusters of costly metals, to incorporate schemes of plasmonics. Sputtering had been used to produce textured surfaces of TCOs, used in SCs [10]. However, a systematic research is needed to study sizes of nano clusters as a function of sputtering parameters, substrate temperature and ambient conditions to maximize \( \eta \), using concepts of plasmonics. Oxide formation of nano metallic clusters in ambient conditions, hampers the study of actual size, such as formation of GaOₓ on GaAs, InOₓ on InP etc. Hence, study of nano clusters under in-situ conditions is required. In the present work, formation of nano clusters of Sn and SnOₓ on SnO₂ as a function of sputtering time is studied using ultraviolet photoelectron spectroscopy (UPS) under in-situ conditions. Atomic force microscopy (AFM) and optical transmission measurements are used in ambient conditions. Results of these studies are given below.

2. Experimental:
Commercial F doped SnO₂ thin films deposited on glass have been used for present study. SnO₂ films, cleaned with acetone were loaded in the preparation chamber. UPS spectra had been measured on angle integrated photoelectron spectroscopy (AIPES) beam line of INDUS-1 synchrotron source. Vacuum in the AIPES experimental chamber was better than 2x10⁻⁹ Torr. Other details of AIPES experimental chambers are given in previously published paper [21]. Ar⁺ ions sputtering was done at 2x10⁻⁵ Torr partial pressure of argon, at room temperature, in the preparation chamber separated by the gate valve from the experimental chamber. Energy of Ar⁺ ions was 500 eV and current was 5 µA. After sputtering, samples were transferred to experimental chamber and UPS spectra were recorded within half an hour after sputtering. Photoelectron counts are collected in steps of 20meV with pass energy of 20eV. Polycrystalline Au foil was also loaded along with SnO₂ samples. UPS spectrum from the Au foil is used as a reference to characterize the monochromatic synchrotron light and the Fermi energy level (EF) of the metallic sample holder.

AFM studies were done to measure sizes of clusters on the surface of sputtered samples after taking out samples to ambient conditions. Surface topographies of 10 minutes sputtered SnO₂ samples were imaged using a multimode scanning probe microscope (NT-MDT, SOLVER-PRO).
AFM measurements were carried out in a non-contact mode using silicon cantilever tips having radius of curvature ~ 20nm and a spring constant 5.5 N/m with a resonant frequency of 190 KHz under ambient conditions. Top surface was electrical grounded during measurements. Mean length and width of individual nano clusters were estimated using the imaging software (SOLVER-PRO). Analysis was carried out at various places on the surface of samples. Transmission spectra of un-sputtered and sputtered SnO2 films were measured in the range 200nm-1000nm (VARIAN, CARY5000).

3. Results and Discussion

3.1 Photoelectron Spectroscopy:
SCs deposited on transparent substrates such as ordinary glass and polymers have one electrode usually of thin film of TCO. For example, incident light enters through TCO in p-i-n solar cells of amorphous silicon hydrogen alloy (a-Si:H) and micro-crystalline silicon hydrogen (µc Si:H) [10]. Patterned Ag layer and nano clusters of noble metals (Ag, Au etc) had been used, at the interface of bottom electrode and semiconductor layer, to enhance the absorption of incident light [2,3]. Can nano clusters of constituent elements of TCO play similar role to that of noble metals? This is a research topic and worth exploring. UPS spectra of sputtered surfaces of SnO2 had been measured to study the presence of nano clusters of Sn and SnOx. UPS spectra of SnO2 film measured with incident energy of 100eV are shown in figure 1. Curves 1(black), 2(red) and 3(blue) show spectra of un-sputtered, 3 minutes sputtered and 15 minutes sputtered surfaces of SnO2 film. Arrows V1 and V2 show valence band onset of un-sputtered and sputtered surfaces.

The difference between the Fermi level (EF) and the valence band onset (Vb) of un-sputtered surface (= EF -Vb) is 3.3±0.05eV. EF - Vb of 3 minutes and 15 minutes sputtered surfaces are 2.7±0.05eV and they are same within error levels. There are two possible causes for this difference between un-sputtered and sputtered surfaces.
Figure 2. Curves 1, 2 and 3 are same as in fig.1. (a) Sn-4d core spectra of un-sputtered and sputtered surfaces, (b) Valence Band Plasmons peaks of un-sputtered and sputtered surfaces.

First cause is that there is more upward band bending at the sputtered surfaces resulting in the reduction of \((E_F - V_b)\). Second cause is that the optical band gap \((E_g)\) of top layers after sputtering is less than \(E_g\) of un-sputtered surface. Any one of these or both will reduce \((E_F - V_b)\). This information is important in theoretical calculation of \(\eta\) of SCs and it is discussed after comparing with transmission spectra of un-sputtered and sputtered SnO\(_2\) thin films.

Figure 2 (a) shows expanded UPS spectra of Sn-4d core level and (b) shows expanded UPS spectra due to bulk plasmons of un-sputtered and sputtered surfaces. Curves 1, 2 and 3 in figure 2 are same as in figure 1. The ratio of intensity of Sn-4d peak to intensity of O-2p is increasing as a function of sputtering time. This shows that the concentration of Sn is increasing after sputtering. The origin of bulk plasmons peaks at higher binding energies (B.E.) in UPS spectra (figure 2) is due to reduction of kinetic energy (K.E.) of core photoelectrons by scattering with plasmons [15]. The difference between the B.E. of scattered photoelectrons by plasmons and B.E. of core elastically scattered photoelectrons is equal to the energy of plasmons. A comparison of present UPS spectra with published UPS and electron energy loss spectra (EELS) of Sn, SnO and SnO\(_2\) helps in assigning the origin of various peaks in figure 2(b) [15, 20]. The broad peak at 18eV in the UPS spectrum of un-sputtered surface is due to VBPs of SnO\(_2\). Broad plasmon peaks near 10 and 14eV in UPS spectra of sputtered surfaces, (curves 2 and 3 in figure 2 (b)), can have contributions from clusters of both SnO and metallic Sn. Reported plasmon peaks at 13.5 and 9 eV are due to bulk and surface components of VBPs of SnO. Plasmon peaks at 14 and 10 eV in UPS spectra of sputtered surfaces are due to bulk and surface components of FBPs of metallic Sn. The intensities of peaks near 14 and 10 eV are increasing as...
sputtering time is increased. Clearly, UPS spectra of sputtered surfaces show presence of both Sn and SnO.

3.2 Transmission and AFM studies:

Transmission spectra of un-sputtered and sputtered SnO2 thin films are shown in figure 3. There is no noticeable difference in the transmission spectra of un-sputtered and sputtered SnO2 films. Transmission spectra were measured within half an hour after taking out sputtered film in ambient room conditions. Oxidation of nano clusters of metallic Sn into oxides in ambient conditions makes it difficult to differentiate between sputtered and un-sputtered thin films by transmission measurements in ex-situ conditions [17]. Hence, in-situ measured UPS spectra are more useful to study the effect of sputtering. The origin of the observed decrease in the difference (EF – Vb) in UPS spectra after sputtering, figure 1, can not be answered definitely as the difference on transmission spectra of un-sputtered and sputtered SnO2 thin films is very small. Increase in the upward band bending at the sputtered surface looks more probable, but more studies carried out in in-situ conditions after sputtering will resolve this issue.

AFM 2D pictures of un-sputtered and 10 min. sputtered surfaces of SnO2 thin films are shown in figure 4(a) and (b) respectively. The un-sputtered surface shows grains of size ~ 200nm. Few smaller size grains are also visible. RMS roughness is ~ 28nm. The main difference between the 10min. sputtered and the un-sputtered sample is the appearance of large number of small size (~ 30 – 50nm) clusters sitting over the underneath large size grains. The rms roughness of the sputtered surface remains nearly same. It appears that these nano clusters are formed due to preferential oxygen sputtering from the surface.
Textured surfaces of TCOs, prepared by sputtering without breaking vacuum in fabrication line had been used in SCs [10]. The role of nano clusters had not been considered in the performance of SCs. Present results indicate that nano clusters of Sn, SnOx are present at the sputtered surface. Distribution of sizes of nano clusters of Sn, SnOx and SnO2 depends upon the sputtering conditions and duration of sputtering. If one can deposit nano clusters of SnO2 of appropriate sizes such that their surface components of FBPs are in the energy range 0.5 - 1.5eV, then these will be useful in enhancing the absorption of incident radiation in the sub band gap region of semiconductors with band gap less than 1.5eV such as c-Si, a:Si:H, µc:SiH thin films, GaAs etc. Energy of plasmons of nano clusters of diameters (d) more than about 50nm is independent of size, however it increases as 1/d^2 for sizes less than 50nm [22]. It is a topic of further research to measure energy of FBPs of nano clusters of TCO as a function of size, so that they will be useful in enhancing $\eta$ of SCs. This will be a cost effective process as sputtering equipments are already in use in the fabrication line.

4. Conclusions

UPS spectra of sputtered SnO2 thin films show presence of nano clusters of Sn and SnOx at the surface. There is very little change in transmission spectra of un-sputtered and sputtered SnO2 thin films, measured in ambient conditions. AFM studies show grains of average size 200nm on un-sputtered surface and formation of nano clusters of average size 30-50nm sitting over the underneath large size grains after sputtering. It is proposed that plasmons due to free carriers in nano clusters of SnOx of sizes less than 10nm can be used in SCs to increase absorption of incident light in the energy range 0.5-1.5eV.

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