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Optical evaluation of doping concentration in SiO_2 doping source layer for silicon quantum dot materials

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Abstract We have investigated and proposed a simple method to correlate optical absorption with high B doping concentrations in thin SiO_2 films that offer a potential doping source for Si quantum dots. SiO_2 films with boron and phosphorus were deposited using a computer controlled co-sputtering system. By assessing the absorption coefficients, it was observed that the doping can dramatically increase the absorption of the transparent SiO_2. Additionally, the highly doped SiO_2 films have a very broad Urbach like absorption tail and the absorption corresponds well with the doping level.

1 Introduction

The use of silicon quantum dots (QD) in photovoltaic has been proposed as a means to develop an all-silicon tandem solar cell. This third generation solar cell concept, involving depositing superlattice materials with Si quantum dots embedded in dielectric materials (SiO_2, Si_3N_4 or SiC), has been previously investigated [1]. A p-i-n structure has already been fabricated demonstrating a device with rectifying characteristics [2]. Doping is one critical requirement for device fabrication. Using dopant rich SiO_2 layers as the doping source for diffusing boron or phosphorous into the superlattice is found to change the conductivity of layers containing QDs [3]. This method has an advantage over the typical in-situ way of doping during film deposition because in-situ doped B or P in SRO layer influence the quantum dot formation and QD size control becomes difficult [4,5]. Therefore research interest is drawn to these highly doped SiO_2 film focusing on controlling the concentration and the diffusion as well as its optical properties.

Due to the insulating property of thin SiO_2 films, the doping level of this material cannot be evaluated simply through electrical measurement. Meanwhile, although there are many advanced material analysis approaches for thin film layers, such as SIMS and RBS, they are not suitable for quick examination of the doping concentration. In this work we attempt to correlate the optical properties and doping concentration to find a possible method to analyze doped SiO_2 films quickly.

To achieve this goal, we deposited SiO_2 films on quartz substrates with by co-sputering boron and phosphorus with various concentrations. This work could be helpful for researchers working on quantum dot materials and those who may want to utilize doped insulator layers as doping sources in any other material system.

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2 Experimental

In this work, the SiO_2 doping source layers with various boron and phosphorus concentrations were deposited using a computer-controlled AJA ATC-2200 co-sputtering system. The films were sputtered from a 99.999% silica 4 inch target at a nominal rate of 1.5 nm/min using a 135 W of a 13.56 MHz AC in an Ar atmosphere at 1.5 mTorr. Doping was achieved by varying the RF power applied to 2 inch dopant targets. We investigated 48 W, 98 W and 196 W on a Boron target (Metal Boron) and 18 W, 36 W and 72 W on a phosphorus target (P_2O_5). The concentration of dopants is proportional to the RF power used based on the deposition rate of B and P_2O_5. In order to keep the constant SiO_2 matrix, the power on SIO_2 target was fixed. The SiO_2 stoichiometry change will be very small so this effect is only minor effect on absorption comparing to highly doping. X-ray Reflectivity (XRR) was used to accurately measure the film thickness [6]. The equipment used for XRR is a PANanalytical X'Pert MRD, which has a primary X-ray source of CuKα (λ = 0.154 nm), which is collimated with a divergence slit of 1/4° (divergence of 0.27°). Incident and reflected beams are respectively collimated by two Soller slits with 2.3° divergence. A 1/32° anti-scatter slit was used to improve the resolution of the detection by PIXcel3D detector configured in "receiving slit" mode.

The optical characterization was carried out measuring the reflectance and transmittance of the films

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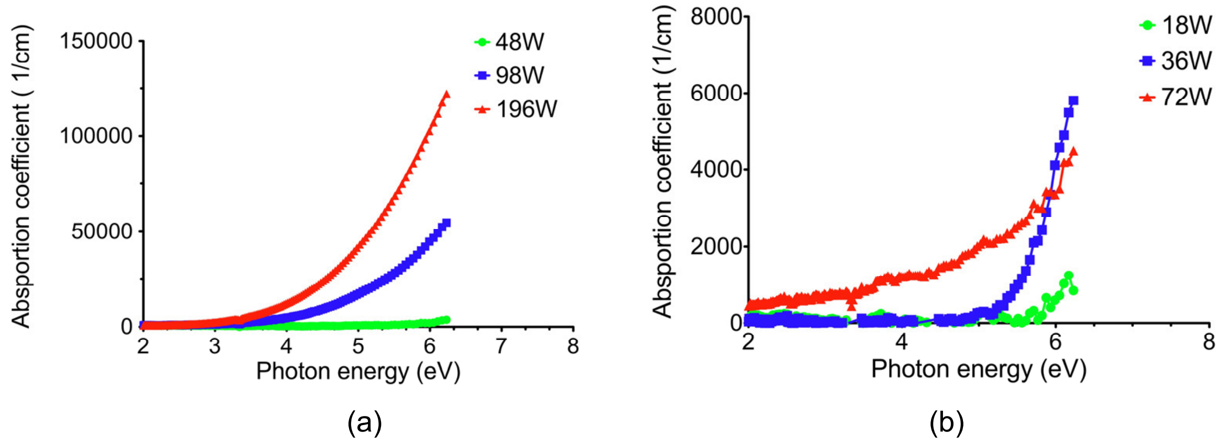

Fig. 1. Absorption results of Boron (a) and Phosphorus (b) doped samples are different. Boron has clear absorption relationship with doping level while Phosphorus loses the trend in higher power doping.

Table 1. Thickness measured by XRR and refractive index determined by optical simulation.

Sample	Thickness (nm)	Refractive Index (n)
Boron 48 W	37.6	1.442
Boron 98 W	40.7	1.468
Boron 196 W	48.3	1.617
Phosphorus 18 W	40.0	1.444
Phosphorus 36 W	45.8	1.451
Phosphorus 72 W	60.8	1.474

on quartz substrate using a Lambda1050 PerkinElmer UV/VIS Spectroscopy. A photomultiplier Tube (PMT) detector was used for the 200 nm to 860 nm range and an InGaAs photodiode detector was used for the 800 nm to 2000 nm range. To determine the absorbance of the films, R and T were measured and the absorption coefficient was found as suggested by Maley [7], so that the absorption coefficient can be evaluated simply without iterative procedures. The Cauchy model, usually used for transparent semiconductor, was applied to evaluate the refractive index of the film by modeling T only.

Finally, two samples were examined by XPS. One sample is doped with Boron using 98 W on the Boron target and the other is phosphorus doped using 36 W on the P_2O_5 target. The measurement was carried out using an ESCALAB220i-XL system with an Al Kα X-ray source.

3 Results and discussion

The films thickness was designed to be around 40 nm. However due to the high boron and phosphorus sputtering rates the thickness increases proportionally with the power used on the dopant targets. In Table 1, the refractive index at 600 nm from simulation with Cauchy model shows that the Boron doped samples have a stronger change than phosphorus doped samples. The Cauchy model was applied for simulating T for the non-absorption region of the spectrum. The accuracy of the simulation was improved by using the XRR measured thickness, avoiding the need to also fit this parameter. It manifests that refractive index increases with doping level.

The absorption coefficient results were evaluated according to N. Maley's approach [7]. The optical properties of the substrate (quartz) are known therefore the R and T on the surface can be easily calculated by using the known index of refraction "n". The equations [7] used for calculating the absorption coefficient are,

$$\begin{cases} T = \frac{T_{sa}T_f}{(1-R_{sa}R_f)} \\ R = R_{sa} + \frac{T_{sa}^2 R_f}{(1-R_{sa}R_f)} \\ \frac{T_f}{1-R_f} = \frac{(1-R_{fa})e^{-ad}}{(1-R_{fa}^2 e^{-2ad})}. \end{cases} \quad (1)$$

Where T and R are the transmittance from the film side and reflectance from the substrate side respectively. T_{sa} and R_{sa} represent the transmittance and reflectance from the substrate/air interface, which can be calculated from the known "n" of quartz. R_{fa} represents the film/air reflectance. But R_{fa} has a minor effect on the absorption coefficient result in practice according to Maley here we used the modeling results at 600 nm for calculation.

According to the absorption results in Figure 1, both boron and phosphorus doped samples exhibit higher absorption starting from the photon energy over 4 eV compared to that of bare SiO_2 (9 eV). The absorption increases proportionally with sputtering power, which is proportional to the doping level. By comparing two doping types, the boron doped samples have much higher absorption than the phosphorus doped ones. The XPS results showed that boron sample (98 W) has 10 at% concentration is much higher than phosphorus (36 W) with 2 at.%. So boron samples must have relatively higher concentration, which could explain the higher absorption since doping concentration is basically proportional to the sputtering power. What should be noticed in the Boron doped sample's absorption curves is that they have a very regular increment with increasing sputtering power. On the other hand, among the phosphorus doped samples the trend deviates when the power reaches 72 W. But it is still clear that the absorption increases significantly over the whole

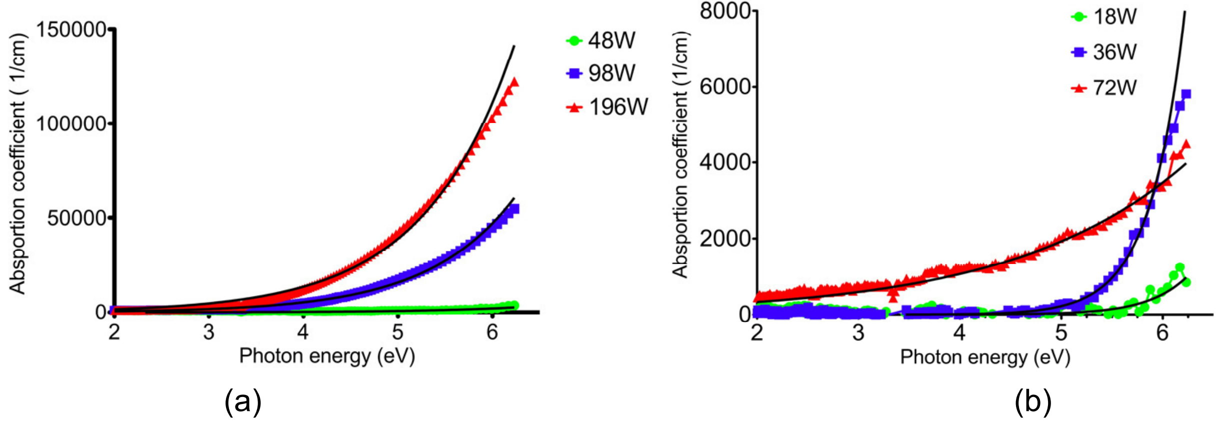

Fig. 2. Graph (a) is B doped samples' absorption with good fitting in exponential curve. Graph (b) is P doped samples only for 18 W and 36 W. 72 W P doped sample has very different absorption curve. It is hard to get good exponential fitting for Phosphorus doped samples because the absorption is quite weak.

Table 2. Doping concentration predicted according to the relation.

Sample	α	k	Tauc edge
Boron 48 W	5.2	1.00	4.7 eV
Boron 98 W	67.8	1.09	5.1 eV
Boron 196 W	203.4	1.05	4.8 eV
Phosphorus 18 W	8.28e-5	2.6	5.5 eV
Phosphorus 36 W	9.44e-5	2.9	5.4 eV
Phosphorus 72 W	101.7	0.59	4.6 eV

spectrum. It should be mentioned that the PerkinElmer UV/VIS Spectroscopy gave negative absorption values therefore the absorption coefficient is upward shifted by $1000\,\text{cm}^{-1}$ offset. The negative value is due to a systematic error in R/T measurement from the PerkinElmer UV/VIS Spectroscopy. Additionally, the absorption in Phosphorus doped SiO_2 samples is much smaller than T and R since the film is only 40−60 nm. However, the trend is still obvious that absorption is proportional to doping level.

The spectrum range from 4 eV to 6 eV for boron and 5.5 eV to 6 eV for phosphorus were selected for curve fitting in order to overcome lower absorption region that gives more error points making it hard to fit curves. In the case of boron, we can fit curves well by using an exponential function $Y = \alpha e^{kx}$ (Fig. 2(a) and Table 2), however fitting accuracy decreases if we include higher photon energy spectrum. Phosphorus doped samples (Fig. 2(b)) did not show very good fittings (lower R-square) due to the weak absorption which has larger noise. It can be seen that for all the spectrums $E > 6$ eV, the fitting curve deviate from data points. This indicates that Tauc region should be over 6 eV. The P 72 W doped sample has a very broad absorption region compared to the samples doped using lower sputtering power. The reason for this effect is not clear yet This change for high P concentration might be caused by that more defects generated and different kinds of defects might exist.

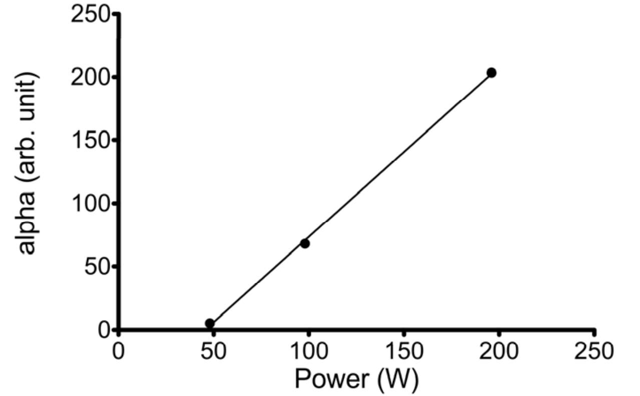

Fig. 3. Boron doped samples exhibit linear relationship between sputtering power and α.

Comparing α values from fitting, which represents the intensity, it is not possible to correlate concentration with absorption in P doped samples because they have very different k values. On the contrary, Boron doped samples exhibits similar k values thus there is obvious trend in α values (Table 2). We can find a linear relationship between sputtering power and α (Fig. 3). Therefore it might be possible to simply correlate α with doping concentration that is proportional to the sputtering power for B doped SiO_2 But it is not effective for P doped samples especially for higher doping level. In order to quantify the doping centration, RBS or SIMS will be necessary.

It is obvious that higher doping B and P into SiO_2 dramatically enhance the absorption. Generally it is believed that the dopants will form distinct energy levels as Giusy et al. observed in PL/PLE measurement on phosphorus doped silica [8] and Dong et al. also tried to simulate energy levels for different III/V dopants by using first principle calculation on substitutional dopants in SiO_2 materials [9]. However in this experiment it is not likely to be the case that the dopants will form constant defect energy levels within the bandgap. Because if we try

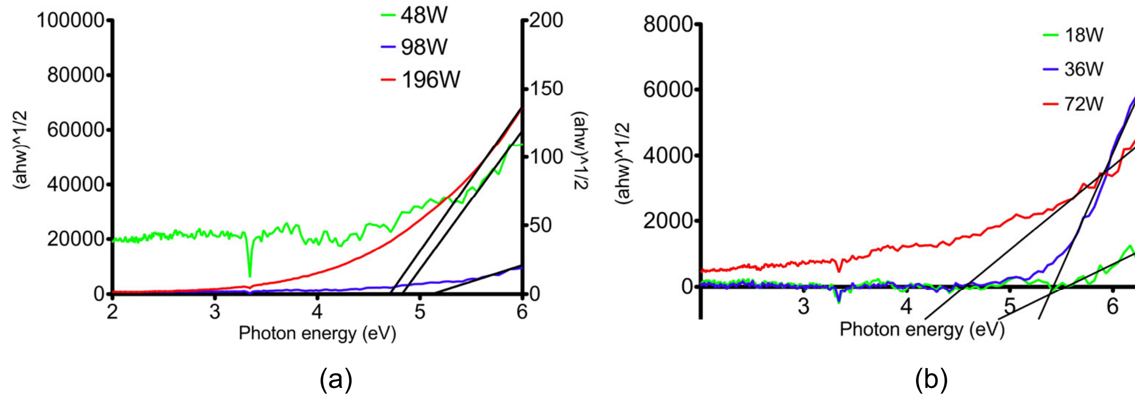

Fig. 4. Tauc plot for Boron (a) and Phosphorus (b) doped samples. 5−6 eV was used for linear fitting. It is clear that X intercepts are very different. Boron 48 W has very low absorption therefore use secondary Y-axis.

to consider that the high energy region has a Tauc plot shape $(ah\omega)^n$, the doped samples should show similar absorption edges independent of doping level. But according to our measurements this is not the case. Here we use $n = 2$ as generally used value, the Tauc absorption edge varies from 5.1 eV to 4.7 eV for boron-doped samples and from 5.5 eV to 4.6 eV for the phosphorous-doped samples (Figs. 4(a) and 4(b)). But it might be necessary for us to extend the optical absorption spectrum to higher energy region to show more accurate Tauc plot and also apply PL measurement to see whether the defect levels really exist.

Urbach tail region following Tauc region is usually manifest in amorphous materials and it is usually related to disorder, impurity and defects. The absorption curves in our case have very Urbach-like shape so it is helpful to interpret the overall trend in the absorption by applying Urbach theory, such as doping induced defects [10]. Additionally, from the fact that P doped samples have very different k values rather than similar k values as B doped samples, which usually represents Urbach energy, it might be the clue that P forms more different and complex bonds network or defects than B. In order to investigate more details on this disordered material from doping, it requires more accurate characterization methods such as by FTIR, PDS or even EPR [11]. Such characterization techniques are beyond what this paper is aiming to present. Here a very simple model could be used to explain the trends we observed.

But it might be easier to apply a simple model to explain the higher absorption with increasing doping level. If we consider the amorphous material mixed with dopants as "condensed solution" we can then apply Beer's law ($\alpha = \varepsilon C d$) that can concisely represent the relationship between the concentration and absorption. C represents defects concentration, d represents film thickness and ε represents absorption cross-section. The absorption is proportional to the defects which means more absorption sites and it is believed to be proportional to doping level.

4 Conclusion

In this paper, we proposed and examine one rapid way to examine the high doping level in SiO_2 thin films by simply evaluating optical absorption. It was found that boron doped SiO_2 exhibits a well proportional relationship between doping level and absorption. However phosphorus doped samples did not show this relationship. More accurate measurements on absorption and doping concentration will be further needed to verify the results in this paper.

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