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Preparation and multiple exciton generation of hydrogenated nanocrystalline silicon film prepared at different powers

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Abstract. The nc-Si:H films prepared by PECVD under different powers was characterized by Raman spectra, XRD pattern, and transmission measurements. The XRD pattern displays that the nc-Si:H nanocrystallites films is successfully prepared on quartz glass substrates. The average grain sizes of the prepared samples at different powers were estimated from full width at half maximum of (111) peak. The optical band gap of nc-Si:H films indicate that the optical band gap can be modulated by power. In the end, a simple statistical model was used to explain the effect of multiple exciton generation in the prepared nc-Si:H semiconductor material. The results indicate that multiple exciton generation efficiency in nc-Si:H film is related with both the size of quantum dots and incident photon energy.

1. Introduction
Currently, researches on the thin-film solar cells with low cost and high efficiency have aroused the increasing interest. Multiple exciton generation (MEG), as an important effect in nano semiconductor, can be used to enhance the efficiency of solar cell devices because absorbing a high energy photon can create the multiple electron-hole pairs [1-3]. So far, many experimental researches have been shown the existence of highly efficient MEG in semiconductor nanostructures or quantum dots, including, PbSe [4, 5], PbS [6, 7], Si [8] and so on. In addition, MEG in semiconductor nanocrystals has been explained by some theoretics, such as virtual exciton generation approach, coherent multie exciton model, atomistic model, and so on [9-11]. Su et al. had well explained the MEG effects in PbSe quantum dots by a simple statistical model based on the framework of Fermi statistical theory and impact ionization [12].

It is well known that hydrogenated nanocrystalline silicon (nc-Si:H) is a two-phase mixed materials, i.e. nanocrystals embedded in the amorphous silicon matrix. This structure means that it has several inherent advantages, such as the strong optical absorption, high carrier mobility, tunable bandgap and good stability. Therefore, nc-Si:H film has received great attention for its potential application in photovoltaic cells. In addition, the existing Si quantum dots in the amorphous silicon matrix also could yield the MEG effects, which could prompt the formation of electron-hole pairs to improve the
efficiency of photovoltaic cells. However, there is a limited research on MEG in the nc-Si:H films. In this manuscript, the nc-Si:H films have been prepared by hydrogen diluted silane PECVD methods at different powers. We have investigated in details on the influence of the powers on the film properties and MEG.

2. Experimental set-up
The nc-Si:H thin films were prepared on the quartz glass substrates by PEVCD system with 13.56 MHz radio-frequency. During deposition, the pressure and substrate temperature were maintained at 100 Pa and 200°C, respectively. Silane (SiH₄) and hydrogen (H₂) was used as the source gases, where the hydrogen dilution rate (SiH₄/(SiH₄+H₂)) was kept constant at 1%. Keeping all these parameters constant, we grew the samples on the glass substrates with the various powers of 60, 70, 80, and 90 W, respectively. The structural properties of the synthesized samples were determined using the X-ray diffraction (XRD, X’Pert Pro with Cu Ka of 1.5406 Å). Raman spectra were recorded by a Jobin Yvon LabRAM HR UV-NIR micro-Raman system under 488 nm laser excitation. Transmission spectra were measured by using spectrophotometer (UV-2550).

3. Results and discussion
To investigate the structural properties of the nc-Si:H thin films prepared at different powers, we carried out XRD measurement. Figure 1(a) shows XRD pattern of the nc-Si:H thin films fabricated at 80 W. It displays two diffraction peaks at 2θ = 28.2° and 47.2°, which is corresponding to the (111) and (220) crystallographic orientations of c-Si, respectively [13]. The broadening of diffraction peak related with c-Si phase indicates that a number of silicon nanocrystalline embed the prepared thin film. The strongest XRD peak intensity for the (111) plane shows that the nanocrystallites have preferentially grown along the (111) direction. The average grain sizes of the prepared samples at different powers were estimated from full width at half maximum of (111) peak using well-known Debye-Scherrer equation. Figure 1(b) shows the calculated average crystallite sizes between 6.2 and 8.5 nm with the increase of powers.

![Figure 1.](image)

Figure 1. (a) and (c) XRD pattern of the nc-Si:H thin films fabricated at 80 W. (b) the power-dependent grain size and band gap.

Figure 1(c) shows the measured transmission spectra for the samples prepared at 80 W. If we ignore the reflected light, the absorption coefficient can be calculated by the equation \( \alpha, T \), and \( d \) is absorption coefficient, transmission and the film’s thickness, respectively. The optical band gap \( E_g \) of the prepared nc-Si:H films can be estimated by Tayl’s methods [14]. Figure 1(b) also shows the optical band gap \( E_g \) of the samples prepared at different powers. With the increase of power from 60 to 90 W, The optical gap of nanocrystalline silicon rise in gradual. The optical properties of nc-Si:H films can be greatly affected by many factors, including the ratio of volume fraction (c-Si, a-Si, and voids), surface effect, hydrogen content, quantum size effect, and so on [13]. It is still lacking a complete microscopic understanding of band gap depended on the microstructure in the films. However, the present observations clearly indicate that the optical band gap can be modulated by power.
According to Yukawa’s meson theory, the collision between two high-energy nuclei will produce many elementary particles. In order to study this process of these elementary particles’ generation, Fermi built a statistical model [15]. And MEG process is similar to it in some aspect because the multiple electron–hole pairs in the nanometer semiconductor are also generated by impact ionization after collisions. Therefore we can refer to Fermi statistical model to establish a new statistical model of MEG in the nano semiconductor materials.

The absorption of a single photon of high-energy $h\nu > E_g$ (h is the Planck constant, $\nu$ photon frequency and QDs band gap $E_g$) will generate an electron–hole pair (or an exciton) in semiconductor. And when $h\nu > 2E_g$, the nascent photogenerated charge carriers will generate the second exciton by collision with other bound electrons, which is so-called impact ionization [16]. If the new generated charge carriers have enough kinetic energy. It will generate more excitons. In the process, the regional volume of incident photon to release its energy is incident photon energy relaxation volume $\Omega$.

According to the effective mass approximation theory, the electron-hole pair kinetic energy can be shown as a function of the velocity $v$. The relationship between the band gap $E_g$ of Si and should be content to the function. The semiconductor band gap and quantum size must have close relationship.

According to the Brus equation [17, 18], we can establish an empirical equation by fitting the experimental observation, as shown in figure 2(a). It can be expressed as,

$$E_g = 1.69 + \frac{3.98}{d^{1.36}} - \frac{0.19}{d}$$

Figure 2. (a) The dependence of band gap $E_g$ on the particle size. (b) the $I_{QE}$ at different particle size and photon energy.

Where the fitted value 1.69 is the band gap of amorphous silicon, and $d$ is the diameter of Si quantum dots. The fitting parameter -1.36 is in agreement with results of -1.37 [19]. With the increasing size of Si quantum dots, the band gap of nc-Si:H films will decrease.

The electron and hole release its energy in the crystal lattice whose mean free path is $l_p$ ($l_p = 0.466nm$ in Si crystal). Then in $t_e$, the maximum energy relaxation length $l_{MAX} = \sqrt{l_p v t_e / 2}$. Therefore, the maximum photon relaxation volume relaxation volume $V_{pr}$ can be expressed as $V_{pr} = \pi l_{MAX}^3 / 6 = \pi (l_p v t_e / 2)^{3/2} / 6$. The electron and hole can’t move out nano semiconductor, so $\Omega$ should be $\Omega = \min(V_{pr}, V)$. $V$ is the volume of nano semiconductor. In the nano semiconductor materials of volume $V$, when it absorbs a high-energy photon of energy $hv$ and then produces $n$ independent quasi-free particles [20, 21], the momentum of the $n$ particles are $P_1, P_2, P_3, \ldots, P_n$. Then the probability $p(n)$ and the energy state density $S(n)$ of the end equilibrium state can be described as [12],
In equation (2), the reduced Planck constant $\hbar$ can be expressed as, $\hbar = h / 2\pi = 1.055$ (unit: $10^{-34}$ J $\cdot$ s). $Q(E_{ks})$ is 3n-dimensional momentum space volume of the system total kinetic energy of the particles. According to the relationship between the total kinetic energy and particles mass $m_1, m_2, m_3, \ldots, m_n$, the $S(n)$ in equation (2) can be expressed as [12],

$$S(n) = 2 \times \left( \frac{m_1 m_2 m_3 \cdots m_n}{2^{3n/2}} \pi^{3n/2} \hbar^{3n} \right)^{3/2} \frac{V^n}{n^{3n/2-1}} \frac{E_{ks}^{3n/2-1}}{(3n/2-1)!}$$

When nano semiconductor whose band gap $E_g$ is absorbs photon energy of $h \nu$ and produces $n$ particles, and the total kinetic energy of the particles can be expressed as:

$$E_{ks} = h \nu - \frac{n E_g}{2}$$

Therefore, the statistical weight can be written as:

$$\alpha(n) = p(n) \times S(n) = 2 \times \left( \frac{m_1 m_2 m_3 \cdots m_n}{2^{3n/2}} \pi^{3n/2} \hbar^{3n} \right)^{3/2} \frac{V^n}{n^{3n/2-1}} \frac{E_{ks}^{3n/2-1}}{(3n/2-1)!}$$

When the semiconductor nanoparticle whose band gap $E_g$ absorbs a single photon whose energy is $h \nu$, it can produce electron-hole pairs whose maximum number is $N_e = [h \nu / E_g]$. So nano semiconductor materials absorbs a high-energy photon and produces particles whose relative probability $W(n)$ can be calculated by the equation as follows [12]:

$$W(n) = \alpha(n) / \sum_{n=2,\ldots,2N} \alpha(n), \quad (n = 2, \ldots, 2N)$$

According to equation (6) and statistical theory, nano semiconductor absorbs a high-energy photon and produces electron-hole pairs whose statistical average $\langle N_{sa} \rangle$ can be expressed as [12]:

$$\langle N_{sa} \rangle = \frac{1}{2} \sum_{n=2,\ldots,2N} n W(n)$$

Nano semiconductor absorbs a singe photon [18] and produces the number of electron-hole pairs in its inner. This is the definition of MEG efficiency $I_{QE}$ effect in the semiconductor materials. And it can be expressed as:

$$I_{QE} = \langle N_{sa} \rangle \times 100\%$$

According to the above equations, we can draw the following curve when it absorbs photons with different energy, i.e. 3 eV, 3.5 eV, 4 eV, 4.5 eV, and 6 eV. Figure 2(b) showed the relationship of MEG efficiency IQE and particle size. For a given incident light, IQE firstly is increasing with the rise of Si quantum dot diameter. In addition, it can be observed that for a given quantum dots, the larger the photo energy, the higher the MEG efficiency. The present results indicate that IQE in nc-Si:H film is related with both the size of quantum dots and incident photon energy.
4. Summary
In summary, we have investigated the influence of the power on microstructure and optical properties of the nc-Si:H films prepared by PECVD through Raman spectra, XRD pattern, and transmission measurements in details. The strongest XRD peak intensity for the (111) plane shows that the nanocrystallites have preferentially grown along the (111) direction. The average grain sizes of the prepared samples at different powers were estimated from full width at half maximum of (111) peak using well-known Debye-Scherrer equation. The optical band gap of nc-Si:H films indicate that the optical band gap can be modulated by power. In the end, a simple statistical model was used to explain MEG in the prepared nc-Si:H semiconductor material. The results indicate that IQE in nc-Si:H film is related with both the size of quantum dots and incident photon energy.

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References
[1] Beard M C and Ellingson R J 2008 Laser Photonics Rev. 2 377-99
[2] Conibeer G 2007 Mater. Today 10 42-50
[3] Nozik A J 2002 Physica E 14 115-20
[4] Schaller R D and Klimov V I 2004 Phys. Rev. Lett. 92 186601-4
[5] Ji M B, Park S, Connor S T, Mokari T, Cui Y and Gaffney K J, 2009 Nano Lett. 9 1217-22
[6] Ellingson R J, Beard M C, Johnson J C, Yu P R, Micic O I, Nozik A J, Shabaev A and Efros A L 2005 Nano Lett. 5 865-71
[7] Schaller R D, Sykora M, Pietryga J M and Klimov V I 2006 Nano Lett. 6 424-9
[8] Beard M C, Knutsen K P, Yu P R, Luther J M, Song Q, Metzger W K, Ellingson R J and Nozik A J 2007 Nano Lett. 7 2506-12
[9] Schaller R D, Agranovich V M and Klimov V I 2005 Nat. Phys. 1 189-94
[10] Shabaev A, Efros A L and Nozik A J 2006 Nano Lett. 6 2856-63
[11] Franceschetti A, An J M and Zunger A 2006 Nano Lett. 6 2191-5
[12] Su W A and Shen W Z, 2012 Solid State Commun. 152 798-801
[13] Parashar A, Kumar S, Gope J, Rauthan C M S, Dixit P N and Hashmi S A, 2010 Sol. Energy Mater. Sol. Cells 94 892-9
[14] Tauc J, Grigorovici R and Vancu A 1966 Phys. Stat. Solid. (b) 15 627-37
[15] Fermi E 1950 Prog. Theor. Phys. 5 570-83
[16] Tauc J 1959 J. Phys. Chem. Solids 8 219-23
[17] Brus L 1986 IEEE J. Quan. Elec. 22 1909-14
[18] Brus L 1986 J. Phys. Chem. 90 2555-60
[19] Wang L W and Zunger A, 1994 J. Phys. Chem. 98 2158-65
[20] Hu Y Z, Lindberg M and Koch S W 1990 Phys. Rev. B 42 1713-23
[21] Yoffe A D 1993 Adv. Phys. 42 173-266