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Characterization of doped hydrogenated nanocrystalline silicon films prepared by plasma enhanced chemical vapour deposition*

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The B- and P-doped hydrogenated nanocrystalline silicon films (nc-Si:H) are prepared by plasma-enhanced chemical vapour deposition (PECVD). The microstructures of doped nc-Si:H films are carefully and systematically characterized by using high resolution electron microscopy (HREM), Raman scattering, x-ray diffraction (XRD), Auger electron spectroscopy (AES), and resonant nucleus reaction (RNR). The results show that as the doping concentration of PH_3 increases, the average grain size (d) tends to decrease and the crystalline volume percentage (X_c) increases simultaneously. For the B-doped samples, as the doping concentration of B_2H_6 increases, no obvious change in the value of d is observed, but the value of X_c is found to decrease. This is especially apparent in the case of heavy B_2H_6 doped samples, where the films change from nanocrystalline to amorphous.

Keywords: PECVD，doped hydrogenated nanocrystalline silicon film，microstructure
PACC: 8115H, 6855, 7360F

1. Introduction

Solid nanocrystalline materials have received a great deal of attention due to their special structures and characteristics.[1] In semiconductor systems, the two-dimensional films,[2] one-dimensional nanowires[3] and zero-dimensional quantum dots[4] have been active research subjects. The hydrogenated nanocrystalline silicon films (nc-Si:H) are nanocrystalline materials that are composed of approximately 50% nanocrystalline silicon grains and 50% amorphous silicon in the interface region between grains.[5] Consequently, the nc-Si:H films possess similar features to those of crystalline silicon; whereas nanocrystalline silicon grains are distributed disorderedly, so a large number of interface regions show their particular structures and bonding styles. In recent years many groups have prepared high-quality films by using various techniques, and many interesting results have been reported.[6] The nc-Si:H films have been revealed to possess very promising electronic and optical properties. Some research papers have reported that nano-crystalline silicon grains with a size of 3–6 nm in nc-Si:H films possess quantum dot (QD) characteristics in both their micro-structures and electrical properties. The high conductivity of the films comes mainly from conduction through the grains, while the interfaces are essentially insulated.[7] The conduction mechanism of the nc-Si:H film, which is called heterojunction quantum dots tunnelling mechanism, is quite different from that of common semiconducting materials. Thereby, the conductivity at room temperature ($\sigma = 10^{-3}$–10^{-1}) of the nc-Si:H film is 1000 times higher than that of the c-Si:H material. On this basis, we have developed tunnelling diode devices from nc-Si:H thin layers (around 20 nm in thickness), and observed resonant tunnelling, negative differential conductance (NDC), and quantum step phenomena in the σ–V, I–V and C–V characteristic curves at a liquid nitrogen temperature or below (<100 K).[8] Based on these results we believe that nc-Si:H films have quantum transport characteristics and potential applications in the fields of Si-based photo-electricity devices and quantum functional devices. Recently, one has clearly revealed that the doping of phosphorus can enhance the conductivity of nc-Si:H by two orders, so it is necessary to study the microstructure and effect in the doped nc-Si:H films in hopes of further exploring the novel physical properties of this kind of material.

Recently, through vapour phase doping we have prepared P-doped nc-Si:H films and studied their microstructures and electric properties. It is found that

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the grain size of P-doped nc-Si:H film is about 2.5–4.5 nm, which is smaller than that of nc-Si:H films. The conductivity of P-doped nc-Si:H film is in the range of 10^{-1}–$10^{1}\,\mathrm{cm}^{-1}$, two orders of magnitude higher than that of nc-Si:H films.[9] Since doping can effectively control both the model of conduction and the conductivity, controllable doping is important for application in photo-electricity and quantum functional devices.

In the present study, phosphorus- and boron-doped nc-Si:H films are prepared by using plasma-enhanced chemical vapour deposition (PECVD). The microstructures and components of the P- and B-doped nc-Si:H films are studied systematically by using high resolution electron microscopy (HREM), Raman scattering, x-ray diffraction (XRD), Auger electron spectroscopy (AES), resonant nucleus reaction (RNR) and other various methods.

2. Experiment

2.1. Sample preparation

The doped nc-Si:H films are prepared in a conventional PECVD system. Initially, the background pressure reaches 1×10^{-4} Pa. The gas-supplying system consists of the mass flow meter, which controls the gas-flow rate. Through the tiny openings in the parallel electrode plates, the gases flow into the deposition chamber afterwards are pumped out through a mechanical pump set. The pumping speed is controlled through the throttle, the total gas pressure in the chamber is kept constant during the deposition. The substrates are located on the upper electrode plate. The heater for the substrates consists of the eight tungsten-iodide lamps, each with a power of 500 W, which are arranged around the side of the upper plate. The spacing between parallel electrode plates can be controlled. A DC potential is applied across the parallel electrodes to provide a negative bias, and an RF voltage with a frequency of 13.56 MHz is applied between the electrodes to ionize the gas into electrons and ions. To avoid the interference between of the direct current and the radio frequency signal, the two power suppliers are isolated electrically by the capacitance and inductance between the electrodes. Based on previous deposition technology,[8] the doping of the nc-Si:H film is performed from the high hydrogen-diluted silane with phosphorus alkane (PH_3) or borane (B_2H_6), whose concentrations are 5%, 0.5%, and 0.3% separately. The doping volume ratios of PH_3 and B_2H_6 to silane are varied from 10^{-3} to 10^{-1}. The technological parameters selected are as follows: an electrode spacing of 25 mm, an background vacuum pressure of 10^{-4} Pa, a substrate temperature of 150–250 °C, an RF power of 20–100 W, a DC bias voltage ranging from −100 to −250 V, a gas flow rate SiH_4/ (PH_3 or B_2H_6 + SiH_4+H_2) of less than 1%, and reaction gas pressures of 90 Pa and 133 Pa. During each test, the films deposited simultaneously on three kinds of substrates: glass substrate, quartz wafer, and monocrystalline silicon wafer. The deposition rate is found to be dependent on gas doping ratio. The depositing time is 6–10 h and the thickness of film is around 1 μm. Prior to the reaction, hydrogen flowing into the chamber is stimulated to emit the light, which irradiates the substrate surface for 10–15 min thereby the substrate surface is cleaned by etching. Once the reaction is finished, the doping process is completed. Hydrogen continues to flow into the chamber for 10–15 minutes more in order to eliminate some weak bonds on the film surface and to decrease the fault appearance and the dangling bonds, which ensures high-quality films forming and there doping.

2.2. Analysis

Impurity content and hydrogen content in the doped nc-Si:H films are measured and analysed by using ϕ500 multi-purposes Auger electron spectroscopy (AES) and resonance nucleus reaction (RNR). The HREM microstructure images of the films are taken by using the JEM-4000EX at a working voltage of 400 kV and atom resolution of 0.19 nm. The Raman scattering spectra by the scattering on the test light route is tested at room temperature, the test system employs the argon ion laser beam (514.5 nm), of which the power is 30 MW. The x-Ray diffraction images are taken by using the Rigaku diffraction instrument (Cu KαL), and choosing film annex to improve the signal noise ratio and accuracy. Besides depositing the doped nc-Si:H films on monocrystalline silicon substrate for HREM microstructure analysis, we deposit the doped nc-Si:H films also on glass substrate and quartz wafer substrate for other microstructure analysers. Hence, the systematic research and analysis of microstructures of nc-Si:H films doped by distinct impurities can be conducted.

3. Results and discussion

The use of high concentration hydrogen diluted silane with phosphorus alkane (PH_3) or borane (B_2H_6) as the reactant gas to grow silicon films in a PECVD system can eliminate the weak Si–Si bonds through the etching effect of the [H] and [P] or [B] radicals in the plasma. Thus the silicon film texture may be improved and silicon atom nucleation can be promoted. High-quality B- and P-doped hydrogenated nanocrystalline silicon films with nano-phase morphology have been produced by using the method.

Figure 1 is an HREM image of phosphorus doped nc-Si:H films sample.

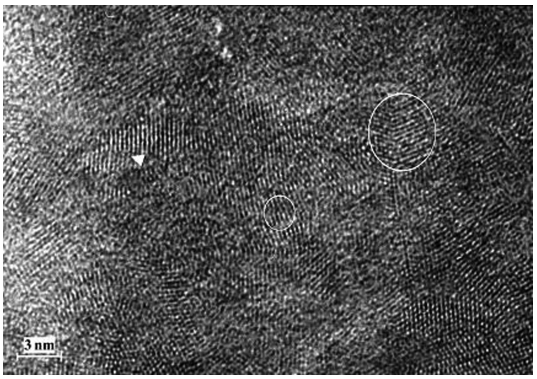


Fig.1. The HREM microstructure image of P-doped nc-Si:H film.

The parameters during deposition are as follows: phosphorus concentration (doping volume ratio between PH_3 and silane) 5×10^{-2}, substrate temperature 150 °C, RF power 60 W and DC bias −150 V, reaction pressure of the total gases 90 Pa. From this image, we can find the nanostructure in the film. The mean grain size can be estimated at 2–4 nm and the orientations of the grains are rather random, which are quite unlike what are seen from the image of a-Si:H or μ-Si:H film. There are abundant interfaces between the grains, and the thickness is around 2–4 atomic spaces. And the volume ratio between the crystalline grain and the interface region between grains is about 50%. We can also find from the image that the shape of the interfacial regions varies with the size and distribution of the grains, as well as with the orientations. Because the scattering of atoms on electrons is very weak in the interfacial regions, we can hardly obtain any more information about the dopants and the H atoms. Whether there are defects inside the nanocrystallites is an open problem.[10,11] Our studies show that the defects, such as dislocation and fault, do exist in the grains in the phosphorus doped nc-Si:H films. By comparing the HREM images of P-doped and B-doped nc-Si:H films with those of the intrinsic (undoped) samples, we find that the doping of the phosphorus can reduce the size of grains, but the grain size in boron-doped films is somewhat larger, about 5.5 nm.

The AES measurements in Fig.2 show the atomic percentages of phosphorus and silicon in phosphorus-doped nc-Si:H films versus the depth of the atom away from the surface. It is very clearly seen that the curves representing Si and P atoms are almost parallel to the X-axis, i.e. the phosphorus and silica contents are evenly distributed in the whole films. Figure 3 shows the variation of H content in the doped nc-Si:H films with the volume fraction of the doped gases in the reactant gases. Playing the same role as the H atoms do, some doped atoms in the interfacial regions are absorbed and attached to the dangling bonds, causing the hydrogen content in these regions to decrease.

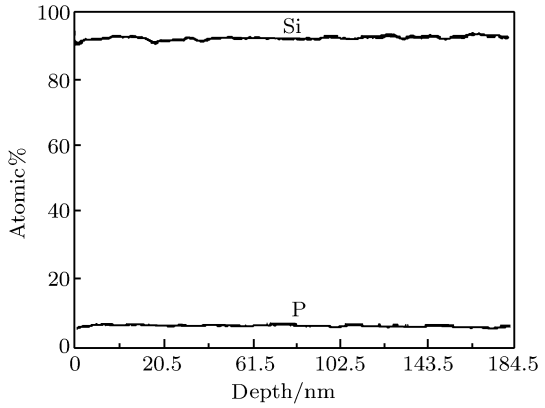


Fig.2. The AES of P-doped nc-Si:H film.

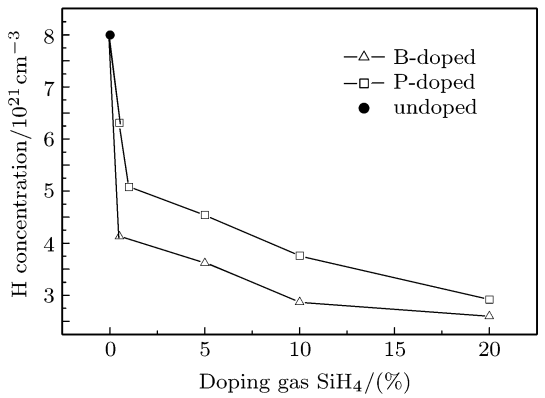


Fig.3. The variation of H content in the doped nc-Si:H films with the volume fraction of the doped gases.

Analysing the differences between the Raman spectra of nano-size materials and other crystalline

materials, we can obtain the structure and bonding style of this material. Figure 4 shows a comparison between the Raman spectra of phosphorus-doped nc-Si:H films and the intrinsic undoped samples. The mean grain size is given by the formula

$$d = 2\pi(B/\Delta\omega)^{1/2},$$

where B is a constant valued $2.21\,\mathrm{nm}^2\cdot\mathrm{cm}^{-1}$, $\Delta\omega$ is the peak shift, the deviation of the measured crystalline peak location from the c-Si peak at $521.5\,\mathrm{cm}^{-1}$. We can also calculate the volume fraction of crystallite from the integrated Raman scattering intensity peak. The samples with different phosphorus content ratios of PH_3/SiH_4: 0, 1×10^{-2}, 5×10^{-2}, and 1×10^{-1}, can give their grain sizes and crystalline volume fractions: 4.6 nm, 48.3%; 3.3 nm, 50%; 2.2 nm, 54.9%; 2.1 nm, 58.1, respectively. This means that the increasing of phosphorous content can effectively restrain the growth of the grains, but the volume fraction of crystallites would increase. Figure 5 shows the Raman spectra of a group of boron-doped samples. Obviously different from Fig.4, the vibration peak location of the crystallites moves a little with the increasing of the boron content, but the grain size remains a value around 5.5 nm. When the boron content reaches 1×10^{-1}, however, it is not easy to observe the peak, i.e. the film has turned into a-Si:H film.

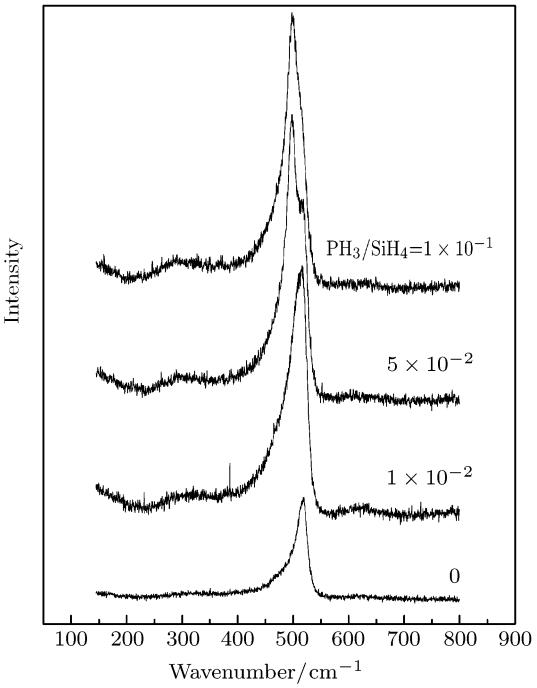


Fig.4. The Raman spectra of a group of phosphorus-doped and undoped samples.

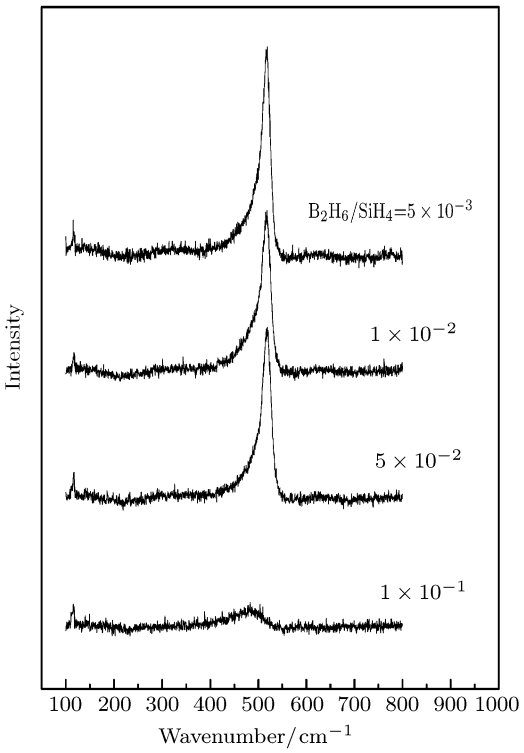


Fig.5. The Raman spectra of a group of boron-doped samples with different phosphorous contents.

In the research on the structure of nanocrystalline materials, x-ray diffraction is one of the most important tools. As is well known, when the grain size is less than 100 nm, the slight grain can broaden the diffraction peak. The relationship between the grain size D and the broaden extent A of the full width at half-maximum of the diffraction peak is given by

$$D = 0.89\lambda/A\cos\theta,$$

where λ is the wavelength of the x-ray. In our experiment, we use the x-ray with $\lambda = 0.154$ nm. And 2θ is the location of the diffraction peak. The mean grain size of the doped nc-Si:H, calculated from both the formula (Scherrer formula) and the broaden extent A of the full width at half-maximum of the (111) peak, is correspondent to that from the Raman scattering. The XRD spectra in Fig.6 show a comparison between a group of P-doped samples that have nearly the same mean grain size but different phosphorous contents (from 0–20%) in the reactant gas. From the figure, we note that the (111), (220) and (311) diffraction peaks in the intrinsic sample are symmetric and sharp, which evidences that the microcrystallites are perfect. But with the increasing of the phosphorous content, (311) peak dies away, while (111) and (220) peaks become

wide and asymmetric. Even more, when the phosphorous content is high enough, the main peak is split into many small peaks, which means the crystal lattice of the micro-grains becoming imperfect. This may be caused by the abundant impurity atoms and defects in the crystallites.

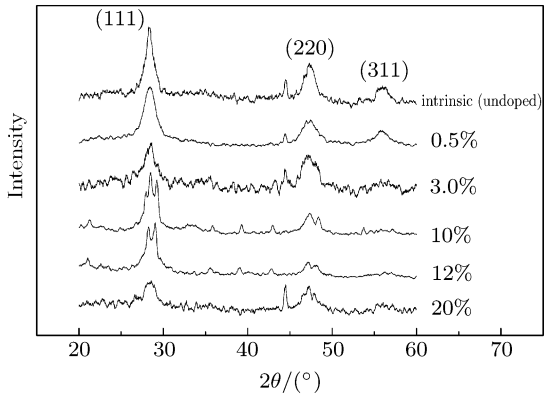


Fig.6. The XRD spectra of P-doped samples with different phosphorous contents.

The XRD spectra of B-doped sample in Fig.7 gives the same result as that of the phosphorous sample. But once the boron content comes up to 10%, the peak no longer exists, i.e. the crystallites are destroyed and the nc-Si:H films have turned to a-Si:H. This also coincides with the conclusion of Raman scattering. Here we try to explain our experimental results from the formation mechanism of the doped nc-Si:H. In the process of P-doped deposition, PH radicals are the dominant resultant, which originate from the dissociation of the doped gas PH_3 by plasma. Then the PH radicals enter the interfacial regions and form the bonding style Si–P–H. Because the bonding energy of P–H is larger than that of Si–H, the P–H bond in the Si–P–H can be easily cut off by the outer energy. In this way, the phosphorous atoms enter the interiors of the crystallites, forming P–Si bonds. So the high concentrations of Si–H and P–H bonds absorbed on the substrate surface can promote the formation of the nano-phase and the effective doping of phosphorous, and then reduce the grain size in the film. The growing mechanism of boron-doped nc-Si:H is similar to that of P-doped sample. Meanwhile, the boron dopant atoms can react with the Si grains to form unsaturated B–Si bonds. These B–Si bonds can be easily filled by atomic hydrogen, resulting in the formation of the neutral B–H–Si complex. Thus the boron atoms can no longer act as an acceptor, and becomes inactive. What is more, as the B–H–Si complex accumulates, the etching effect of the H radical is weakened, which brings on the formation of the B-doped nc-Si:H films with larger grain sizes. Once the boron content (B_2H_6/SiH_4) reaches up to 10%, too many B–H–Si complexes are formed, resulting in the reduction in Si atoms for nucleation, and the nc-Si:H film turn into a-Si:H film.

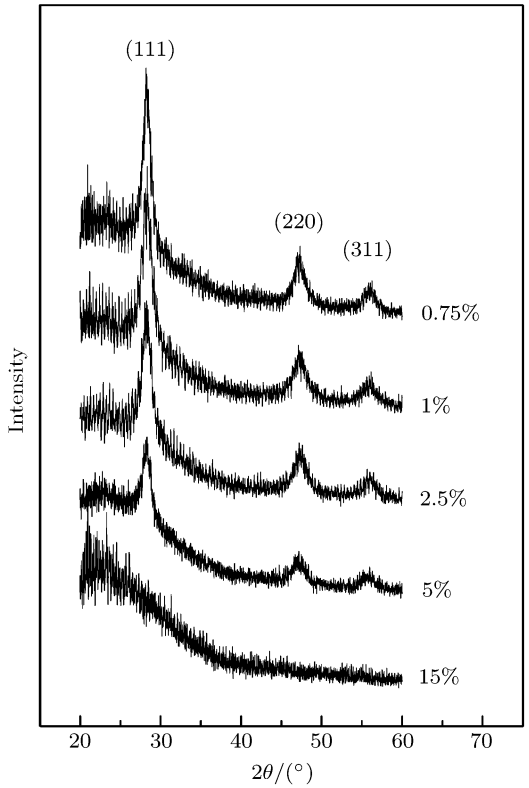


Fig.7. The XRD spectra of boron-doped samples with different boron contents.

4. Conclusion

By analysing AES spectrum and RNR, we find that the content distribution of the elements in the doped nc-Si:H films are well-proportioned. HREM, Raman scattering and x-ray diffraction pattern show that the microstructure of the samples is nano-scaled, even though defects exist inside the crystallites. The mean grain size of the P-doped nc-Si:H films is about 2–4 nm, and the crystalline volume fraction is nearly 50%. But in B-doped nc-Si:H films, the grain size is a little larger (around 5 nm), and the volume ratio between crystalline grain to the amorphous interface is less than that for the P-doped sample case. In addition, with the increasing of the phosphorus content, the grain size of the films diminishes gradually, while the crystalline volume fraction and the grain density

increase. If the dopant is boron, however, the grain size would varies little and the volume fraction of crystallite decreases. But when the boron content reaches some value, the nc-Si:H film turns into a-Si:H one.

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