The influence of annealing on mechanical properties of hydrogenated nanocrystalline silicon thin films

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Abstract: The hydrogenated nanocrystalline silicon (nc-Si:H) thin films were deposited by plasma enhanced chemical vapor deposition (PECVD). The as-deposited films were annealed, and the microstructure and mechanical properties were investigated by XRD, Raman spectra and nanoindenter. The results show that the crystallinity, hardness and elastic modulus have been improved when annealing at 400°C, but the mechanical properties became worse when annealing at 600°C.

1. Introduction
Recently, hydrogenated nanocrystalline silicon (nc-Si:H) thin film, which is compatible with semiconductor technology, has been attractive for their potential applications in light-emitting diodes[1], solar cells[2,3] and thin film transistors[4,5] due to its particular photoelectric properties. Considerable effects including optical and electric properties of nc-Si:H thin films are explored, but little work was on its micro-mechanical properties. The piezo-resistance effect of nc-Si:H thin films have been reported in the previous work[6], and the pressure-sensitive coefficient of the films is 6-8 times than that in monocrystalline silicon. So it is necessary to research and develop high sensitivity micro-pressure sensor, displacement pickup and other micro-nano devices. Moreover, the materials of silicon films have been applied widely in MEMS. Therefore, it is significant for devices application to study the micro-mechanical properties of nc-Si:H thin films. Nanoindentation technique can investigate the micro-mechanical properties such as hardness, elastic modulus and creep and so on[7]. Nanoindentation has pretty high force resolution and motion resolution. With this technique, the changes of burdening and motion can be continuously recorded, making this method a fine way for film mechanical property measurement.

In our previous works, the micromechanical properties of nc-Si:H thin films deposited on different substrates[8] and P-doped[9] had been investigated. The present work mainly studies the influence of annealing on mechanical properties of nc-Si:H thin films. The microstructure of the film was characterized by XRD and Raman scatter spectra. Nanoindenter system was used to measure the mechanical properties of nc-Si:H thin films, e.g., load-depth curve, hardness and Young’s modulus, the effect of annealing process on mechanical properties were researched and the relation between microstructure and micromechanical properties were also probed.

2. Experiments
Nc-Si:H thin films were fabricated on monocrystalline silicon at a radio frequency(13.56 MHz and power 30 W) capacitive coupled PECVD system at a temperature of 260°C and chamber pressure of
0.5 Torr for 9 hours. The working gases are silane (highly diluted by hydrogen, silane 5% and hydrogen 95%) and hydrogen ($H_2$), the gas flow rate (sccm) of silane and $H_2$ are 5 and 45 respectively. Nc-Si:H thin films were annealed in nitrogen atmosphere for an hour at 400°C and 600°C.

The microstructure and crystallinity of the films was measured by Raman spectroscopy and XRD(Cu-Kα1, X-ray wavelength $\lambda=0.15405$nm). The Raman spectra were obtained by micro-Raman equipment using He-Ca laser(325nm) and with a power of 4.5mW, in order to avoid any beam-induced crystallization. Measurements of mechanical properties were performed by nanoindentation with MTS Nano Indenter XP system, using the XP indentation units and accutip indenter; the burdening measuring range is fixed from 0 to 500mN with a resolution of 50nN; the stroke length was 2mm with a resolution 0.01nm. Controlling parameter: strain ratio 0.05/s, heat drift ratio 0.05nm/s, indentation depth 1000nm.

3. Results and discussion

3.1. Microstructure Analysis

Figure 3 shows the XRD diagram of the films. It is found that the diffraction peak (111) of the unannealed film exhibits a weak intensity and an obvious split, indicating that the growth of crystalline grains have a bad orientation. After annealed at 400°C, the intensity of (111) diffraction have been enhanced and the peak is symmetrical, all which mean that crystal lattice orientation becomes finer and more ordered than unannealed film. Crystallite grain-sizes $D$ are calculated using the classical Sherrer formula:

$$D = \frac{0.89 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $\lambda$ is the X-ray(Cu-Kα1) wavelength (0.15405 nm) and $\beta$ is is the half-width peak integral corrected by subtracting the instrumental broadening deduced from the powder reference signal. The average grain-sizes calculated are approximately 5nm at 260°C, 4nm at 400°C and 6.5nm at 600°C, respectively. The results show that the average grain-sizes in film annealed at 400°C is smaller than that in unannealed film. As the diffraction peak intensities increases further, Crystallographic orientation for the film annealed at 600°C get a better order. And that the full width at half maximum(FWHM) decrease sequentially, indicates that the grain-size becomes larger.

The diffraction peak (311) appeared in the annealed films, because the large numbers of hydrogen atoms escaped from the films, resulting in reconstruction of grains and boundaries with the $T_a$ increasing. The fact that there is no the diffraction peak (311) in the XRD spectra, means that the hydrogen atoms don’t have enough energy to overcome potential barrier to readjust interfaces at deposition temperature.
The Raman spectra of the films are shown in figure 2. Analyzing the transverse optical (TO) peak shift and width of the Raman spectra, the grains size \( D \) and crystalline volume fractions \( X_c \) were estimated from empirical formulas\[10\]:

\[
D = 2\pi B \Delta \omega, \quad \text{and} \quad X_c = \frac{I_c}{I_c + \eta I_a}
\]

(2)

where \( B \) is a constant 2.21cm\(^{-1}\)nm\(^2\), \( \Delta \omega \) is the wave-number difference between crystalline (520cm\(^{-1}\)) and amorphous(480cm\(^{-1}\)) TO peak location, \( I_c \) and \( I_a \) are integrated intensities of the crystalline and amorphous, respectively, and the Raman scatter factor \( \eta \) is 1.0 approximately.

We obtained the crystalline volume fraction \( X_c \) and grains size listed in Table 1. It can be found that \( X_c \) nearly change almost while \( D \) decreases after annealing at 400°C. While the \( T_a \) increasing to 600°C, the film’s crystalline volume fraction \( X_c \) increases from 25% to 35.1% and the average grains size from 4nm to 6.5nm. This is in agreement with the results of X-ray diffraction.

| Sample | \( T_a /°C \) | \( X_c \) | \( D \) |
|--------|----------------|--------|-----|
| 1#     | 260\(^{a}\)    | 24.8%  | 5nm |
| 2#     | 400            | 25%    | 4nm |
| 3#     | 600            | 35.1%  | 6.5nm |

\(^{a}\)260°C is the substrate temperature.

3.2. Load-Depth Curve Analysis

Load-depth curves performed on five random points on 1#, 2# and 3# samples at a maximum indentation depth 1000nm are shown in figure 3. There is a distinct “terrace” in one of five curves illustrated in figure 3(a). It is thought that the terrace would be resulted from a crackle or gap existing\[11\] in the 1# film. However no crackle or gap appears at the points in annealed 2# and 3# films because the obvious terrace doesn’t emerge. It implies that the crackle or gap has been eliminated possibly after annealing process.

Five load-depth curves of 2# sample repeat very well, as shown in Figure 3(b). Although there are some differences, the repeatability has been promoted evidently and the maximum loads are close to each other and the residual indentation depths are the same. One can say that the mechanical properties of nc-Si:H thin film has been enhanced by annealing at 400°C. Grains with different size, random holes and higher surface roughness in unannealed film lead to disperse the load-depth curves. Surface features and internal structure have been improved by annealing at 400°C, such as smaller
grain size well-distributed and higher surface smoothness. The average applied load of 2# sample at maximum indentation depths is 160nN and the residual indentation depth is 640nm. The above two mentioned physical quantities hardly changed in comparison with that of unannealed film. All the results state that the resistance to load and elastic recovery are still preserved, and the compatibility of film/substrate deformation has been strengthened at an appropriate $T_a$, for example, 400°C.

### Figure 3. Load-depth curves of samples with different $T_a$: (a) 260°C, (b) 400°C, (c) 600°C.

Load-depth curves of 3# sample were illustrated in Figure 3(c), five curves even more scatter each other. The applied load at maximum indentation depths has a wide range of 125-305nN, which means that the resistance to load is increased at local area and decreased at another local area in the films. Accordingly, the residual indentation depth also has the same tendency, i.e., a great discrepancy comes into being among the elastic recoveries at different points.

#### 3.3. Hardness and Elastic Modulus Analysis

The hardness and elastic modulus versus the nanoindentation depth curves are given in figure 4 and figure 5, respectively. The measured hardness and elastic modulus can’t reliably reflect samples’ properties due to the effect of surface roughness and of the radius of the indenter. It is considered that when the indentation depth is about 10-30% of the film’s thickness[12,13], substrate’s influence could be neglected. So the measured hardness and elastic modulus belong to the nc-Si:H films in the depth range of 80-170nm. The average of hardness and elastic modulus estimated from the curves are given in Table 2.

### Figure 4. Hardness-depth curves of samples with different $T_a$: (a) 260°C, (b) 400°C, (c) 600°C.

We can find that the hardness and elastic modulus increase with the $T_a$ increasing from 260°C to 400°C and 600°C. It indicates that the hardness and elastic would become larger with the $T_a$ raising. Ne-Si:H film is composed of crystalline and amorphous phase. Plentiful hydrogen atoms exist in the
crackles and grain boundaries. Some H atoms escaped from the boundaries and hydrogen content
minishes somewhat at $T_a$=400°C, but most H atoms escaped from the boundaries and hydrogen
content continues to decrease. Because H atom can soften the stress of films [14], hardness raised with
$T_a$ increasing. Therefore hydrogen content is an important factor influencing micromechanical
properties of nc-Si:H thin films.

![Figure 5.](image)

Figure 5. Elastic modulus of samples with different $T_a$: (a) 260°C, (b) 400°C, (c) 600°C.

The hardness-depth curves shown in Figure 4b are more repeatable than shown in figure 4(a) and
figure 4(c), and the elastic modulus curves shown in figure 5(b) have the same change.

| Sample | $T_a$/°C | $H$/GPa | $E$/GPa |
|--------|----------|---------|---------|
| 1#     | 260      | 1.7     | 45      |
| 2#     | 400      | 3.0     | 50      |
| 3#     | 600      | 5.5     | 75      |

The uniformity of micromechanical properties were enhanced for the films annealed at 400°C, but
below or above $T_a$ is adverse to micromechanical properties. The basic cause to the change of
micromechanical properties depends on the microstructure of films. Hydrogen existing in the form of
Si-H hinders Si-Si bond from compact network structure in the films [15]. New Si-Si bond generated
through the anneal process, but several grains unite to be a greater grain at a higher $T_a$ and more gaps
and crackles produced, thereby, the micromechanical properties was influenced. In a word, the
changes of films’ microstructure can explain the differences of micromechanical properties with
varying $T_a$.

4. Conclusion
The surface feature and microstructure of nanocrystalline silicon (nc-Si:H) such as grain size, H
content and distribution of defects are improved by annealing. The mechanical properties are in a
finer uniformity for the films annealed at 400°C, but crystal grains grow largely in size and films’
defects in number when annealing at 600°C, resulting in the decreasing the uniformity of the
mechanical properties of the film.

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