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THE STRUCTURE CHARACTERISTICS AND PIEZO-RESISTANCE EFFECT IN HYDROGENATED NANOCRYSTALLINE SILICON FILMS

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Abstract — In this paper, we successfully applied the PECVD method to deposit nano-crystalline silicon films (nc - Si: H) and determined the microstructure with HREM and STM technology. The nc - Si: H films consist of a large number of micrograins and interfaces. For this man-made film material with special structure, we studied the piezo- resistance effect and hydrogen content, which varied with the microstructure of the films. We suggest that the unique structure of nc - Si:H films is the main cause of larger piezo- resistance effect and higher hydrogen content in the films.

INTRODUCTION

In recent years, we have successfully prepared nanosized crystalline silicon films (nc-Si:H) (1,2), by means of the conventional PECVD method. The nc-Si:H films consist of a large number of fine microcrystallites; the mean grain size is 3 - 6 nm and the crystalline volume fraction is Xc = (53 ± 5) %. The spacing between grains is formed by a great deal of interfaces, as shown in Figure 1. The thickness of interfaces is 1 - 4 atomic layers and the volume fraction of interfaces is about 40%, which is estimated from the HREM picture of Figure 1. Figure 1 is a Fourier filtered image of an HREM picture of a typical nc-Si:H film by using a 486 microcomputer. In these images, a lot of interfaces can be seen more clearly. It is obvious that the microstructure of nc-Si:H films are quite different from C-Si, a-Si:H and μc-Si:H films (3,4).

Recently, scanning tunneling microscopy (STM), which may be used for real-space imaging on a scale with atomic dimensions, has attracted much interest. Some have observed the surface atomic morphology of C-Si (5) and pc - Si (6) (polycrystalline silicon film) with STM. We have employed the CSTM - 9000 type STM, fabricated by the Institute of Chemistry, Academia Sinica, to observe the atomic arrangement in the out-layer surface of nc-Si:H film for the first time (7,8). Figure 2a gives an atomic scale picture of nc-Si:H film, where we can see clearly the distribution of the silicon atoms in the grain and between the grains region. In the lower part of Figure 2a, there exists a grain with size about 1.6 x 3.2 nm, in which the silicon atoms are arranged very regularly. The darker regions around the grain, which are disordered, represent interface regions. Figure 2b
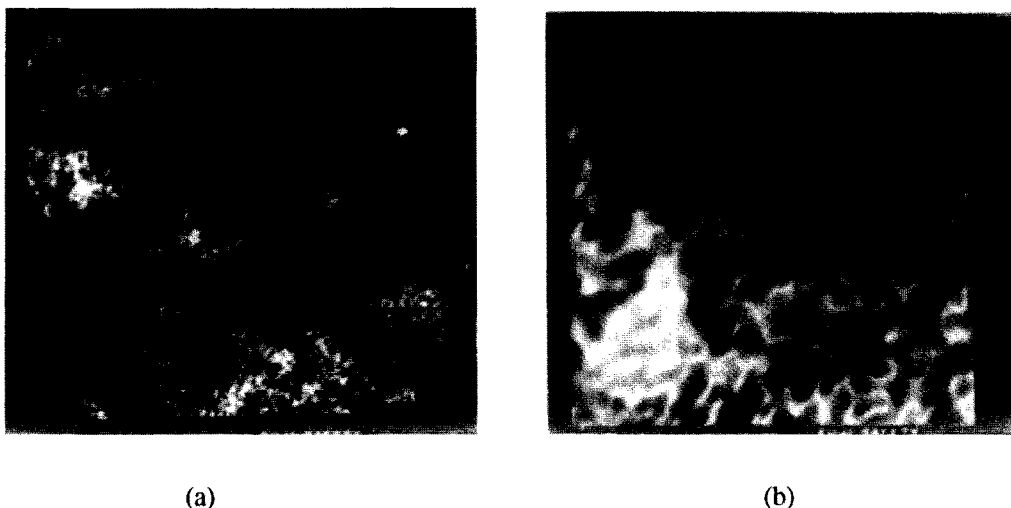
<center>(a)   (b)</center>

Figure 1. Typical HREM picture of nc-Si:H film: (a) original HREM picture, (b) HREM picture after processing by 486 microcomputer.

<center>(a)   (b)</center>
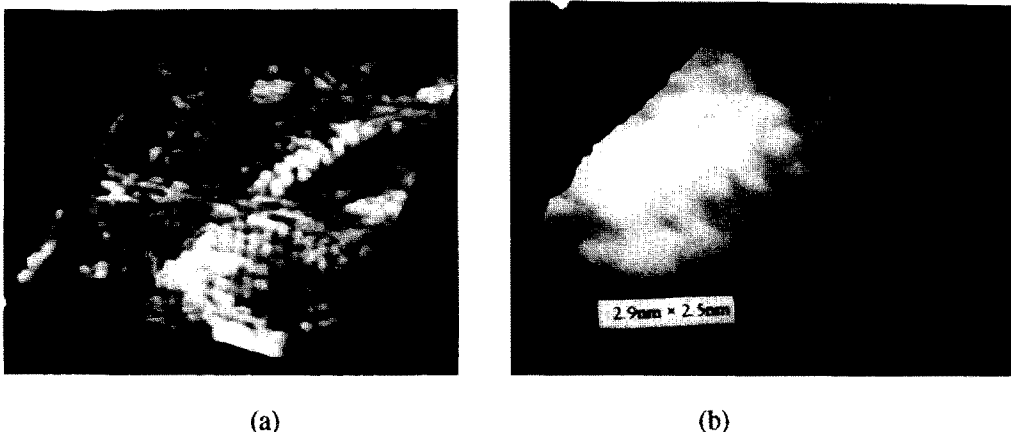
Figure 2. Atomic scale picture of nc-Si:H film by STM: (a) the scanning area is 4.0×5.0 nm^2, (b) the inner arrangement of silicon atoms in a grain.

is the inner arrangement of silicon atoms of a grain. Crystal atoms and interface region atoms are seen in Figure 2. From Figure 2, we can estimate the distance between two adjacent atoms is about 3 Å and the thickness of the interface region is about 1 nm, which is consistent with the HREM picture in Figure 1.

The unique structure characteristics of nc-Si:H films mentioned above cause many novel properties in the films, such as high conductivity ($\sigma_d = 10^{-3} - 10^{-1}$ Ω^{-1} cm^{-1}) and low conductive activation energy ($\Delta E = 0.12 \pm 0.01$ eV)(2), high hydrogen content ($C_H = 20 - 25$ at.%)(2) and

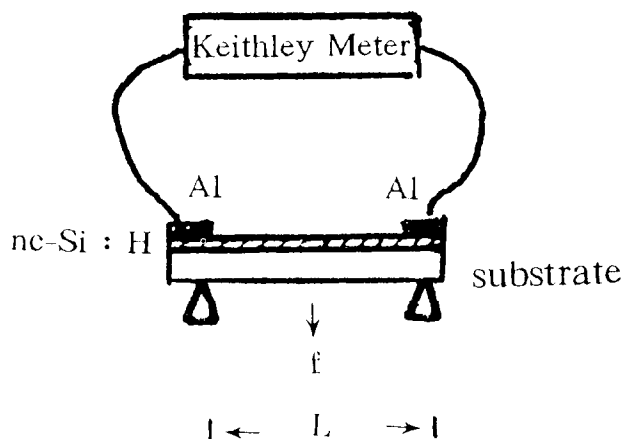Figure 3. A schematic diagram for measurement.

light absorption coefficient α (higher than that of a-Si:H and μc-Si:H in the range of visible and IR spectrum) (9). In this contribution, we focused our attention on the microstructure, piezo-resistance effect and the annealing characteristics of nc-Si:H films.

EXPERIMENTAL DETAIL

The piezo-resistance effect is the physical basis for stress sensors. At present, most of the stress sensors are made of C-Si materials. In general, the strain resistance coefficient K of C-Si is about 20 - 30, but K may be over 100 at a special axis.

In this paper, we used the freely supported beam method to study the piezo- resistance effect of nc-Si:H and μc-Si:H films (10). The measuring equipment is shown in Figure 3. The measured films with its substrates are put on a pair of triangular support holders. We evaporated a layer of Al on two sides of the top of measured films as an electrode, which must be opposite to the support point under the sample. If the measured sample is acted by a force (a standard weight) on the center, the sample will be curved by the force and cause the resistance of the sample to have a variation ΔR.

The changing of curvature and resistance of measured samples under the applied force are measured by a freely supported beam method, which is shown in Figure 3. The nc-Si:H and μc-Si:H films are deposited by an ultrahigh vacuum PECVD system on the glass and quartz substrates. We employed the following formula to calculate the strain resistance coefficient K, which may be used to describe the piezo resistance effect of films (10).

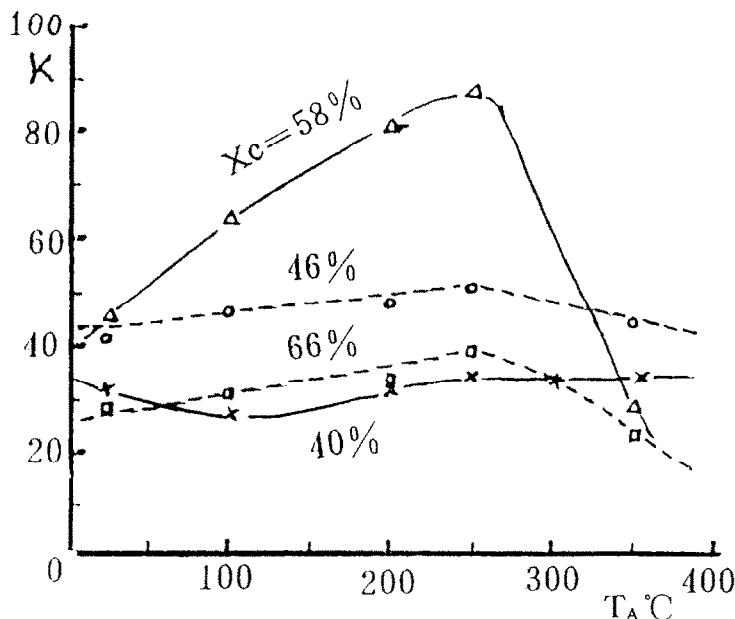$$K = \frac{L^2 \cdot \Delta R}{3t|\Delta Y| \cdot R} \qquad [1]$$

Figure 4. The strain-resistance coefficient K of silicon films as a function of annealing temperature T_A for four different Xc samples.

where L is the distance between two support points, t is the total thickness of measured sample (substrate and film), ΔY is the largest change of curvature at the center point of sample under weight force (standard weights) and $\Delta R/R$ is a value of relative resistance variation of measured film. In our experiment, the values of ΔY are measured by a precision thousandth meter and the data of $\Delta R/R$ are measured with a 617 type Keithley meter.

RESULTS

We employed the freely supported beam method to measure the K values for a series samples of silicon films with different Xc. We classified them to be α-Si (Xc < 30%), μc-Si (Xc = (30 - 47) %), nc-Si (Xc = (48 - 58) %) and pc-Si (Xc > 60%). The Xc values were estimated from Raman scattering spectrum (2). We also studied the effect of the annealing process and found that the K values varied with annealing temperature. For non-annealing samples, the K values at room temperature are Knc > Kμc ≈ Kpc > Kα-Si, as shown in Figure 4. It shows, in the annealing temperature range T_A < 250°C, the K values of nc-Si:H and μc-Si, as well as pc-Si films increased with T_A, particularly for an nc-Si:H sample. Moreover, the K values decreased suddenly as T_A > 250°C. So, there is a optimum annealing temperature at T_A ≈ 250°C. However, the K values remained small and the variation was not detected in the entire annealing temperature range for α-Si:H samples.
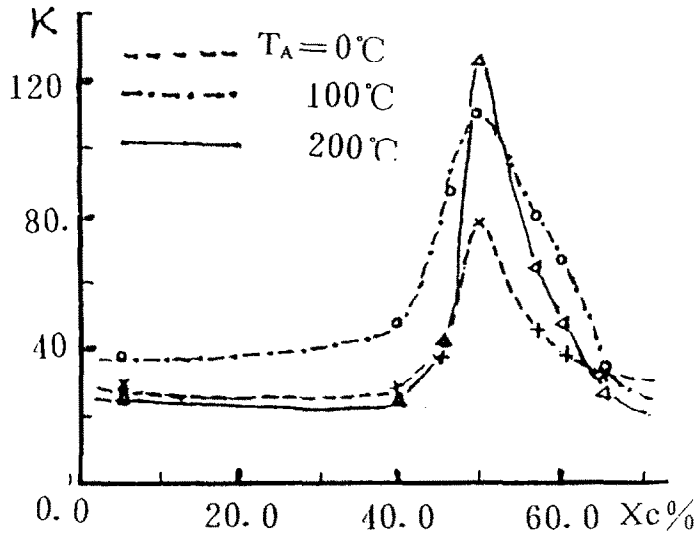
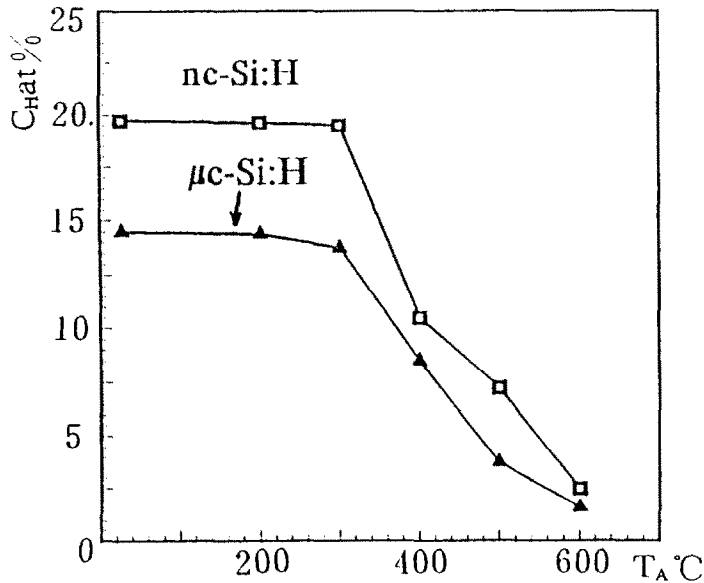Figure 5. The strain-resistance coefficient K of silicon film as a function of Xc for two annealing temperatures.

Figure 6. The hydrogen content C_H of nc-Si:H and μc-Si:H samples varied with annealing temperature T_A.

Figure 5 shows that the K values varied with the crystalline volume fraction Xc for a series of silicon samples. It is shown that the K values remained constant in the range of Xc ≤ 40% (a-Si:H and μc-Si:H regime). It is interesting to note that as the Xc values gradually entered into the

nanocrystalline regime ($Xc \approx 50\%$), the K value elevated suddenly and reached a peak at $Xc \approx 52\%$. Measurements for a series of annealing samples are the same. On the contrary, as Xc further increased, we found that the K value had a sharp decline and restored to the lower level at μc-Si:H regime. The maximum K value of nc-Si:H film reached 130—the largest one for all piezo-resistance materials until now.

On the other hand, we measured the hydrogen content C_H of nc-Si:H and μc-Si:H films by using the resonant nucleation analysis method (11). The hydrogen content C_{II} (at.%) varied with annealing temperature T_A, and the crystalline volume fraction Xc has been drawn in Figures 6 and 7. It is worthy to note that the curve of diagrams in Figures 6 and 7 are very similar to the K value curves in Figures 4 and 5. From Figure 6 we can see that as annealing temperature $T_A \leq 300°C$ the hydrogen content C_H has no evident change. This is evidence that the hydrogen atoms have not released from the films in the temperature range of $T_A \leq 300°C$. But, as annealing temperature $T_A > 300°C$, the hydrogen content C_H obviously decreased, and after 600°C annealing there was only a little content in the films ($C_H < 2$ at.%). So, we consider that the K value lessened as $T_A \geq 300°C$ were related with hydrogen released in this temperature range.

Figure 7 is the volume fraction of crystalline Xc versus hydrogen content C_H for unannealed and annealed silicon films. It shows that the largest value of C_H occurs at $X_c \approx 50\%$, such as the curve of K ~ Xc of Figure 5. This is a new result in this report because as the Xc value increased to ~50%, the microstructure of films entering into nanophase regime and a great deal of interfaces were formed. We consider that the hydrogen atoms will mainly exist in the interface region, as Xc $\approx 50\%$, the density of interfaces is much more in the film (nc-Si:H), so the hydrogen content C_H reached a maximum value. Moreover, the Xc increased continuously and the volume fraction of interfaces Xi decreased, causing the C_H value to drop rapidly.
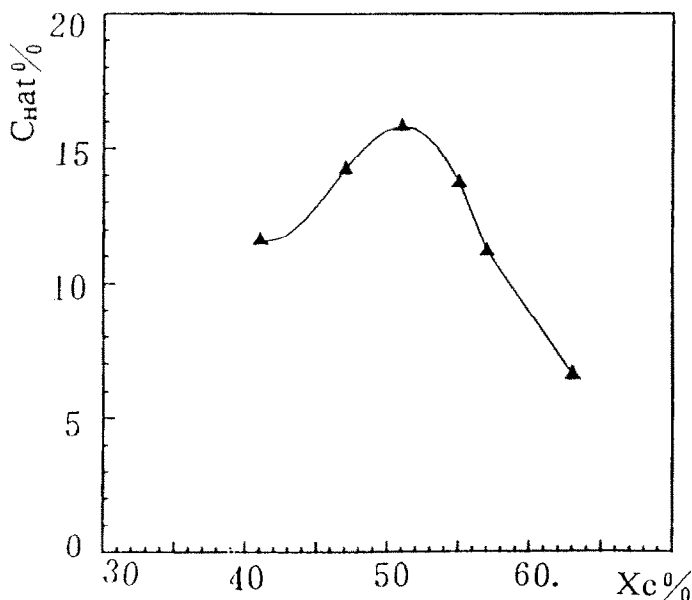

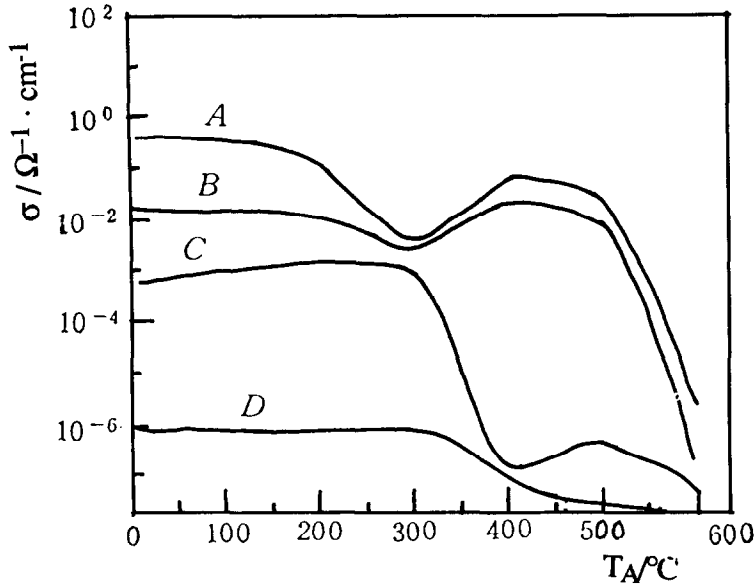Figure 7. The hydrogen content C_H of a series of silicon films varied with Xc.

Figure 8. The relationship between dark room temperature conductivity σ and annealing temperature T_A. Curve A: nc-Si:H (Xc = 0.57); curve B: nc-Si:H (Xc = 0.51); curve C: μc-Si:H (Xc = 0.41); curve D: a-Si:H (Xc < 0.30).
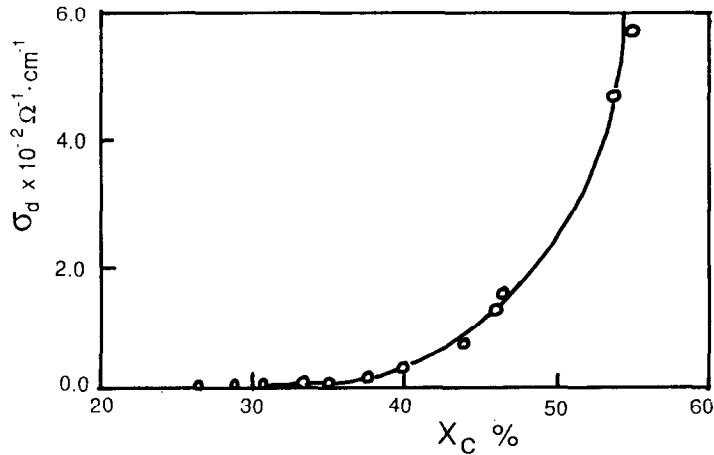
Figure 9. The relationship between dark room temperature conductivity σ and its Xc values.

Furthermore, we also studied the room temperature conductivity σ varied with annealing process for a series of nc-Si:H, μc-Si:H and α-Si:H samples, as shown in Figure 8 (12). We can

see from Figure 8 that for μc-Si:H (curve C) and a-Si:H (curve D) samples, the values appeared slightly elevated, with T_A increasing in the range of $T_A \leq 300°C$, and then made a sudden drop until $T_A \cong 400°C$. But, for the nc-Si:H samples (curves A and B), they slightly decreased in the range of $T_A < 300°C$, and then suddenly rose at $T_A \cong 300°C$. On the other hand, the σ raise point with T_A at $T_A \cong 400°C$ for μc-Si:H (curve C) sample, the three curves (A, B and C) drop again at $T_A \cong 500°C$. It is interesting to note that as $T_A \geq 600°C$, the σ values of three kinds of silicon samples approach an identical level ($\sim 10^{-8} \Omega^{-1} \cdot cm^{-1}$). Compared with Figures 6 and 8, it shows that the C_H values of n-Si:H films sharply decrease as $T_A \geq 300°C$ and then the C_H value approaches zero when $T_A \geq 500°C$. However, as shown in Figure 8, the σ values decrease as $T_A \geq 500°C$. In view of this, we consider that the conductivity σ and its variation have no direct relationship with the hydrogen content C_H for nc-Si:H films.

DISCUSSION

In this paper, we study the piezo-resistance effect and its annealing properties of nc- Si:H films. Simultaneously, we also study the hydrogen content C_H and the conductivity σ varied with its microstructure and annealing process. Because of this, the nc-Si:H films consist of a lot of fine micrograins with a great deal of interface range between grains. There are a mass of silicon and hydrogen atoms loosely and randomly distributed in these interface ranges. Therefore, when an exterior force acts on the films, it must cause a relaxation at the interface range and creates a relative variation of film resistance. We consider that this is a main reason for the largest strain-resistance coefficient K (~130) value of nc-Si:H films. On the other hand, the hydrogen atoms mainly exist in the interface range between grains; therefore, as the density of interfaces is maximized, the hydrogen content C_H is maximized for nc-Si:H films. Most of the hydrogen atoms exist in the interface range, and are compensated with dangling bonds at the surface of grains, constructed to form Si-H_2 and Si - H_3 bonds. Hence, a large number of deep energy levels decrease, accompanied by an increase in the softness of the interface texture. However, the interface texture makes it very sensitive to the action of the exterior stress forces. We can see from Figures 4 and 6 that the variation of hydrogen content C_H and the strain-resistance coefficient K with annealing temperature T_A are nearly the same. This means that the piezo-resistance effect is directly related to hydrogen in nc-Si:H films. As $T_A > 300°C$, the C_H values decrease and cause a decrease in K values also, but the σ value varies unclearly at that time.

In our previous work, we have indicated that the conductivity σ exponentially increases with increasing Xc increasing and apparently raises with the main grain size d decreasing (2,13). This is the so-called small size effect in the conduction mechanism of nc- Si:H films. We have suggested a hetero quantum dots tunneling (HQD) model to explain this phenomena (14). In this paper, we have reported that only the strain-resistance coefficient K varies with the crystalline volume fraction Xc, but have not yet observed how the main grain size d acts on K values. The K value, which is seen in formula [1], is related to the resistivity relative variation $\Delta R/R$ only, but not with the direct variation of σ. Hence, the influence of grain size d is not reflected in the K values. There is a peak in the curve of K - Xc at Xc = 52 %, but there is no peak in the curve of σ - Xc (see Figure 9). Consequently, we consider that the dominant factors acting on the K values are interfaces rather than micrograins in nc-Si:H films.

CONCLUSION

The piezo-resistance effect of nc-Si:H films have been studied. We found that there is a larger strain-resistance coefficient K in hydrogenated nanocrystalline silicon film than other silicon films, such as a-Si:H, μc:Si:H and pc:Si:H. Experimental results show that the K values of nc-Si:H film are directly related to the hydrogen content C_H and its annealing behavior. We suggest that the largest K value of nc-Si:H film comes from the relaxation feature of interface range under the action of exterior forces. Previous work has shown that the conductivity temperature dependence is weakened at a wide temperature region (3,4). So, we consider that hydrogenated nanocrystalline silicon films are ideal man-made materials for the purpose of strain-sensors.

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