Spontaneous generation of negatively charged clusters and their deposition as crystalline films during hot-wire silicon chemical vapor deposition*

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Abstract: The hot-wire silicon chemical vapor deposition (CVD) was approached by the new concept of the theory of charged clusters (TCC). The role of a hot wire is to enhance the rate of negative surface ionization producing negative ions. These ions induce nucleation and produce negatively charged silicon clusters, which deposit as polycrystalline films at low temperatures. During the deposition of silicon, an appreciable amount of negative current ($\sim$nA/cm^2) was measured, and clusters, a few nanometers in size, were captured and observed by transmission electron microscopy (TEM). The effect of bias on the deposition behavior of the clusters indicated that most of the clusters were negatively charged. In order to deposit films with a large grain size with a high mobility, both the generation of neutral clusters and the cluster size should be minimized. A working pressure of 0.3 Torr and a wire temperature of 1800 °C were found to be optimal. Under these conditions, the film with grain size of almost 1 µm could be deposited with a mobility of 175 cm^2/Vsec.

Keywords: silicon; charged clusters; hot wire; chemical vapor deposition; growth mechanism.

INTRODUCTION

Hot-wire or catalytic chemical vapor deposition (CVD) has been studied intensively on account of its unique advantage of crystalline film deposition at low substrate temperatures without the need for plasma [1–3]. However, the underlying principle for the process is unclear. Understanding why crystalline silicon films can grow at low temperatures is essential to its synthesis, which will significantly reduce the trial-and-error methods currently used in optimizing the process. The synthesis of diamond films using the hot wire has been studied extensively [4]. The growth mechanism of silicon hot-wire CVD might be similar to that of diamond hot-wire CVD, particularly in the role of the hot wire.

Hwang et al. [5] suggested the theory of charged clusters (TCC) as a growth mechanism of hot-wire diamond CVD. The TCC states that the negatively charged carbon clusters are generated in the gas phase with their subsequent deposition as diamond films. The existence of negatively charged clusters in the gas phase was experimentally confirmed under typical processing conditions of diamond CVD

[6,7]. The TCC was shown to be applicable to thermal CVD of silicon [8] and zirconia [9]. Besides, thin film growth by charged clusters was found to be general in many thin film processes [10]. In the TCC, the role of the hot wire is to produce the negative ions via surface ionization. The negative ions might act as a nucleation center. This phenomenon is called ion-induced nucleation, which was reported in the historic Wilson cloud chamber experiments in detecting the track of high-energy particles. As a result, the charged nuclei or clusters are formed in the gas phase.

Charged clusters do not coagulate due to Coulomb repulsion and are suspended as nanometer-sized colloidal particles in the gas phase. They are much smaller than the wavelength of visible light and require special techniques for their detection [6]. It is well established in the micrometer-sized colloidal particles that colloidal particles sediment randomly when van der Waals attraction is dominant (flocculation), whereas when the Coulomb repulsion is dominant (deflocculation), they sediment in a highly regular way in a process known as self-assembly [11]. Like micrometer-sized colloidal particles, charged clusters sediment in a highly regular way leading to electrostatic self-assembly into a highly regular three-dimensional array. However, unlike micrometer-sized colloidal particles, charged nanometer-sized clusters leave no voids and undergo epitaxial recrystallization after landing on a growing surface, resulting in perfectly dense films, particularly when the substrate temperature is high enough. Since charged clusters of a small size undergo epitaxial recrystallization on a growing surface, they lose their identity completely. The resulting film does not leave any evidence of its having been assembled by clusters or nanoparticles, which makes it difficult to confirm that the films were grown either by individual atoms or by charged clusters.

In the case of diamond CVD, the sign of the charge has a drastic effect on the film structure [10]. Negatively charged carbon clusters deposit as diamond films, whereas positively charged carbon clusters deposit as hydrogen-containing amorphous films of diamond-like carbon (DLC) when the substrate temperature is low enough to inhibit the hydrogen desorption. The negatively charged clusters tend to be hydrogen free, whereas the positively charged carbon clusters tend to be hydrogenated in the C–H–O system [12].

Although the effect of polarity on the hydrogenation of the silicon clusters has not been studied systematically in silicon CVD, it was suggested that the conclusions made in the carbon system could be applicable to the formation mechanism of amorphous or crystalline films of silicon [10]. As in the case of the hot-wire diamond CVD process, negatively charged silicon clusters are expected to be generated in the gas phase during hot-wire silicon CVD. Negatively charged silicon clusters are expected to be much less hydrogenated and deposit as a crystalline film at relatively low temperatures (<500 °C). In the conventional thermal silicon CVD not using a hot wire, positively charged and thereby hydrogenated silicon clusters are also generated, producing hydrogen-containing amorphous films when deposited at temperatures <600 °C [10].

The first step to check the applicability of the TCC is to measure the electric current generated during the deposition process. Thus far, the generation of electric currents has been confirmed in all thin film processes tested. The charging mechanism in the hot-wire CVD process is believed to be the surface ionization mechanism [13] described by the Saha–Langmuir equation [14]. The second step is to confirm the existence of clusters in the gas phase. The third step is to confirm that the clusters are electrically charged.

The aim of this study was to check the applicability of the TCC to the silicon hot-wire CVD and to determine the optimum conditions needed to deposit the crystalline silicon films with a high mobility at low substrate temperatures.

EXPERIMENTAL PROCEDURE

For current measurements during the hot-wire silicon CVD process, a disc-shaped copper plate with an area of 7 cm^2 was placed 40 mm below the tungsten hot wire. The current was measured as a function

of the wire temperature for three cases: 0.16 Torr under flowing H_2 at 10 standard cubic centimeters per minute (sccm), 0.16 Torr under a flowing gas mixture of SiH_4 (1 sccm) and H_2 (9 sccm), and under vacuum of 5×10^{-6} Torr.

In order to capture the hypothetical negatively charged silicon clusters that were predicted to be formed in the gas phase, a molybdenum transmission electron microscopy (TEM) grid was placed 40 mm below the wire. In order to observe the individual clusters on the membrane of the TEM grid before they coalesce, the time for capture needs to be minimized. The optimum time for capture was found to be 30 s under a flowing gas mixture of SiH_4 (1 sccm) and H_2 (9 sccm) at 0.16 Torr at the wire temperatures of 1500 and 1800 °C. In an attempt to maintain a substrate temperature of 450 °C, the distances between the substrate and the wire were 13 and 40 mm, respectively, for wire temperatures of 1500 and 1800 °C.

To test whether the clusters are electrically charged or not, the electric bias of +150 and –150 V were applied on the TEM grid at the wire temperature of 1500 °C and compared with the case without bias. All other conditions for the bias experiment were the same as those for the cluster capture experiment without bias. The bias was between the substrate holder and the chamber that was grounded.

For a silicon polycrystalline film to have a high mobility, the film should have a large grain size with a minimum defect density. Two conditions need to be met in order to prepare a film with large grain size. One is that deposition of neutral clusters should be minimized (i.e., all the clusters should be charged). The other is that the cluster size should be small enough to allow for epitaxial recrystallization at a given temperature. In order to minimize the production of neutral clusters, the working pressure should be large enough to induce sufficient collisions between charged species and neutral clusters. However, too high pressure would remove the neutral cluster completely, which then makes it difficult for the silicon clusters to deposit on an insulating glass surface. A small amount of neutral clusters is necessary to initiate silicon deposition on a substrate. A reactor pressure of 0.3 Torr was found to be optimal by trial and error.

It should be noted that a pressure of 0.3 Torr is much higher than that used in silicon hot-wire CVD by other groups (0.01~0.05 Torr) [1–3]. Under such low pressure, a relatively large amount of neutral clusters tend to deposit on the substrate, which would initiate silicon deposition easily on a glass substrate, but would decrease the grain size, resulting in a nanocrystalline structure. Besides, neutral clusters tend to produce voids due to random Brownian coagulation or diffusion-limited aggregation on a growing surface.

Since all the silicon flux would be imparted to each negative ion, increasing the percentage of negative ions would decrease the cluster size. Increasing the wire temperature tends to enhance the surface ionization, thereby increasing the generation of negative ions. The wire temperature cannot be too high due to the appreciable evaporation of tungsten silicide. A wire temperature of 1800 °C was chosen to be optimal. The film was deposited for 2 h under a flowing gas mixture of SiH_4 (1 sccm) and H_2 (24 sccm). The temperature of the glass substrate was 450 °C.

The morphology of the deposited film was observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The quality of the films deposited at the wire temperatures of 1800 and 2000 °C was determined by Raman spectroscopy. The Raman result of a single-crystal silicon wafer was used as the reference.

RESULTS AND DISCUSSION

Figure 1 shows the wire temperature dependences of the current measured under a vacuum of 5×10^{-6} Torr, under 0.16 Torr of flowing H_2 (10 sccm) and under 0.16 Torr of a flowing gas mixture of SiH_4 (1 sccm) and H_2 (9 sccm). In all cases, the current was negative. The slight negative current in the vacuum (5×10^{-6} Torr) comes from either electron emission from the wire surface or from the negative surface ionization of the residual gas on the tungsten surface. The negative current measured in the vacuum decreases slightly with increasing temperature at ~1600 °C. This behavior is different from
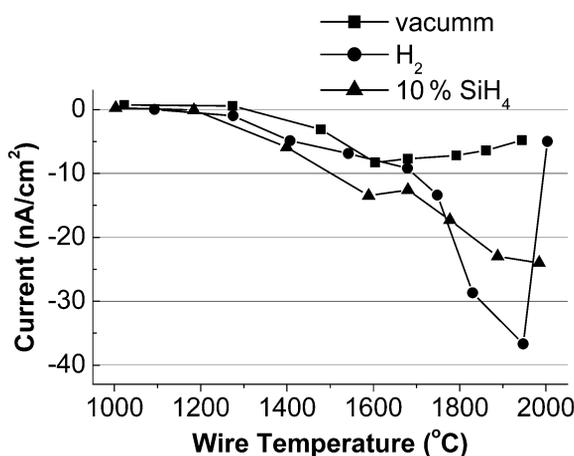
Fig. 1 Temperature dependence of the current measured under a vacuum (5×10^{-6} Torr) and under 01.6 Torr of flowing H_2 and a flowing gas mixture of 10 % SiH_4–90 % H_2.

that expected from the electron emission and might be related to tungsten evaporation or the surface ionization of the residual gas. The negative current data in vacuum can be used as a reference for comparison with the data under flowing gas. It should be noted that the negative current in the vacuum is smaller than that under flowing H_2 or 10 % SiH_4.

Under flowing H_2, the negative current increases with increasing wire temperature up to 1950 °C. However, at a filament temperature of 2000 °C under flowing H_2, the negative current decreases abruptly. The data for the abrupt change at 2000 °C was reproducible. This abrupt change may be related to the evaporation of tungsten. The exact cause has not been determined. Under flowing H_2, the dominant gas would be H_2 with a small amount of atomic hydrogen. Therefore, the dominant species of the negative charge carrier are expected to be hydrogen molecules, which become negatively charged by surface ionization on the tungsten filament.

According to the Saha–Langmuir equation [14], the parameters affecting the surface ionization are the electron affinities of the gas species and the work function of the hot wire because the activation energy for negative surface ionization in the silicon hot-wire CVD process is the work function of the wire minus the electron affinity of the gas species. Among the gas species produced by gas-phase reactions in a mixture of SiH_4 and H_2, those with a relatively high electron affinity are SiH_3 (1.406 eV) and Si_2H_5 (1.49 eV) [15], which are energetically favorable for negative surface ionization on the wire surface. The work functions of pure tungsten and tungsten oxide are 4.5 and 6.24 eV, respectively [15]. The work function of tungsten silicide is not available. The formation of the negative Si_2H_5 ions has been reported in plasma-enhanced CVD [16].

When a gas mixture of SiH_4 and H_2 undergoes gas-phase reactions, the silicon partial pressure builds up, producing a supersaturation for the precipitation of solid silicon, which is equivalent to the driving force for silicon deposition. Therefore, there is a supersaturation in the presence of negative ions produced by the surface ionization at the filament surface. In order to reduce the electrostatic energy of negative ions, the negative ions will attract the supersaturated silicon atoms to produce negatively charged silicon nuclei or clusters. Therefore, the major negative charge carrier for the negative current measured in the flowing gas mixture of SiH_4 and H_2 in Fig. 1 is predicted to be the silicon clusters. A similar analysis was made in the diamond hot-wire CVD process [5], and the predicted negatively charged carbon clusters were experimentally confirmed [7,8].

The hypothetical negatively charged silicon clusters were captured on the carbon membrane of the TEM grid as shown in Figs. 2a and 2b, respectively, at the hot-wire temperatures of 1500 and 1800 °C. The clusters at 1500 °C are larger (~2.5 nm) than those at 1800 °C (~1 nm). Under 0.16 Torr of a flowing gas mixture of SiH_4 (1 sccm) and H_2 (9 sccm), the clusters were captured for 30 s at the grid placed 40 mm below the wire. It should be noted that the prolonged exposure of the TEM grid does not produce a nanostructure consisting of the clusters shown in Fig. 2, but produces a polycrystalline silicon film with a grain size of a few hundreds of nanometers, which is much larger than the size of the original clusters. This result suggests that the small clusters undergo epitaxial recrystallization after deposition and lose their identity completely, making the film grown by clusters almost indistinguishable from a film grown by the atomic or molecular unit.
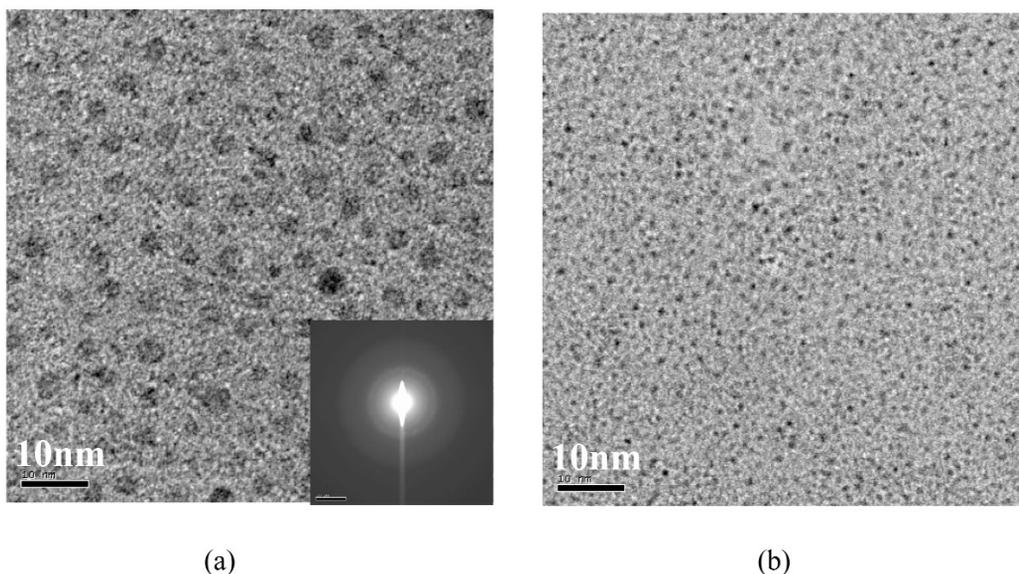

(a)   (b)

Fig. 2 TEM microstructures of clusters captured at the wire temperatures of (a) 1500 °C and (b) 1800 °C. The diffraction pattern in the inset indicates that the clusters are amorphous.

Figures 3a and 3b show the clusters captured at a wire temperature of 1500 °C for 30 s under an applied electric biases of +150 and –150 V on the TEM grid, respectively. There are some clusters on the positively biased grid (Fig. 3a), although the size is much smaller than that on the neutral grid shown in Fig. 2a. In contrast, there were no clusters on the negatively biased grid (Fig. 3b). This indicates that the clusters are negatively charged. When negatively charged clusters are attracted toward the positively biased grid, the mean residence time of the clusters in the gas phase would decrease, resulting in less growth on the clusters compared with that without the applied bias. This would be the reason why the clusters on the positively biased grid (Fig. 3a) are much smaller than those on the neutral one (Fig. 2a) at the wire temperature of 1500 °C. The other conditions were the same as those of Fig. 2.
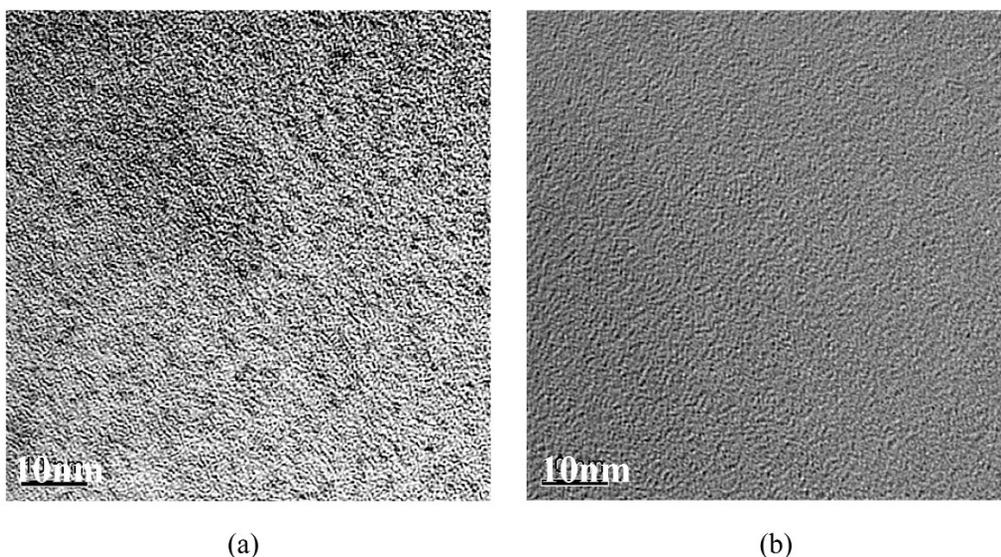
(a)   (b)

Fig. 3 TEM microstructures of the silicon substrates with applied biases of (a) +150 V and (b) −150 V.

Based on the fact that the negatively charged silicon clusters are generated in the gas phase, the low-temperature deposition of crystalline silicon films can be optimized. Although the working pressure of 0.3 Torr and the wire temperature of 1800 °C were chosen to be optimal for a large grain size, deposition did not usually take place on the glass substrate until 30 min. It should be noted that there is no incubation time on a conducting substrate. The difficulty in deposition on an insulating glass reflects the low percentage of neutral clusters, whose condition is necessary for the growth of large grains. Once the silicon deposition was initiated on the glass substrate, the deposition took place at a relatively high rate (~1 μm/h). The difficulty in initiation can be overcome by decreasing the working pressure and/or wire temperature, which would increase the percentage of neutral clusters. Since the charged clusters would mainly contribute to growth, the number density of neutral clusters for initiation would determine the final grain size. Figure 4 shows the relatively large grain size of ~1 μm, which could be obtained by controlling the cluster size and the charging behavior of clusters.
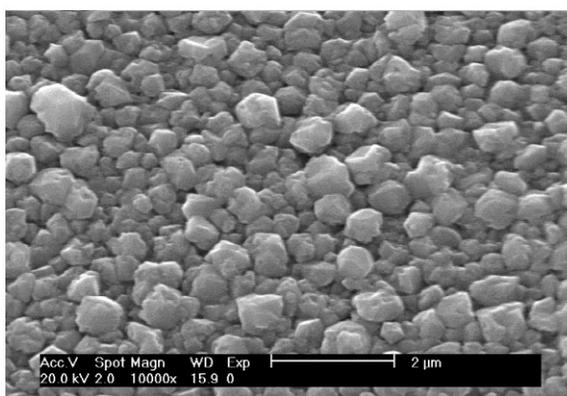

Fig. 4 SEM microstructure on the surface of the film deposited at 0.3 Torr at a wire temperature of 1800 °C with a gas mixture of 4 % SiH_4–96 % H_2. The magnification bar is 2 μm.

Figures 5a and 5b show the AFM microstructures of the film deposited at the wire temperatures of 1800 and 2000 °C, respectively. The surface shown in Fig. 5a is relatively smooth, whereas the surface shown in Fig. 5b is rough with nodules, ~10 nm in size. The rough surface appears to be related to the evaporation of tungsten silicide at 2000 °C. The samples shown in Figs. 5a and 5b were analyzed by Raman spectroscopy to determine the crystalline quality, as shown in Fig. 6. The full width half maximum (FWHM) for the sample at the wire temperature of 2000 °C is narrower than that of 1800 °C. The cluster size would decrease with increasing wire temperature, resulting in larger grain size with decreasing defect density. Therefore, the crystalline quality would increase with increasing wire temperature.
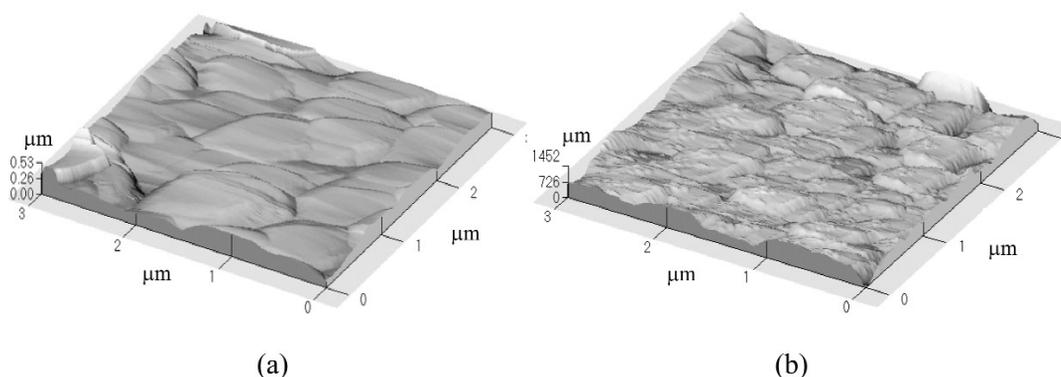

(a)   (b)

Fig. 5 AFM microstructures of films deposited at the wire temperatures of (a) 1800 °C and (b) 2000 °C.
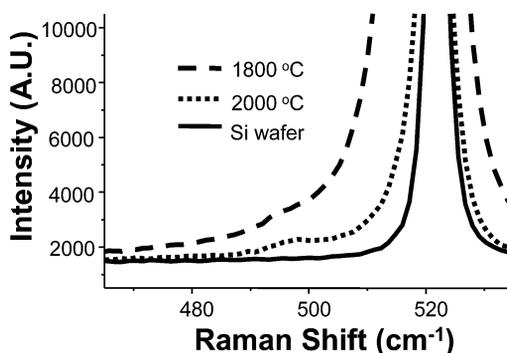

Fig. 6 Raman spectra for the films deposited at wire temperatures of 1800 °C (dashed line) and 2000 °C (dotted line). The solid line shows a Raman spectrum for a single-crystal silicon wafer as a reference.

For the mobility measurement, the sample shown in Figs. 4 or 5a was prepared with a thickness of 1 μm. The resistivity of this sample was 23.57 Ωcm. The Hall effect mobility was 175 cm^2/Vsec with a p-type carrier concentration of 1.5×10^{15}. (The mobility was measured by a standard procedure in LG. Phillips LCD.) This mobility is higher than 70 cm^2/Vsec reported by Matsumura [17]. The possible impurities that can be incorporated in the film are hydrogen and tungsten, which might be responsible for the p-type conductivity.

These results show that the low-temperature deposition of polycrystalline silicon films can be approached systematically based on a new understanding of thin film growth by charged clusters. Although the Raman spectra shown in Fig. 6 indicate that the crystalline quality at the wire temperature of 2000 °C is better than that at the wire temperature of 1800 °C, the mobility of the former is much

lower than that of the latter. The reason might be the incorporation of evaporated tungsten silicide in the film, which would decrease the mobility and increase the carrier density.

Neutral clusters, which are usually harmful to the film, can be avoided by increasing the working pressure. However, in the absence of neutral clusters, the initiation of deposition is difficult on an insulating substrate due to Coulomb repulsion between the insulating surface and the charged clusters. This difficulty in initiation also arises in the deposition of GaN on insulating substrates in the MOCVD process [18]. This effect of the substrate conductivity on the deposition of charged clusters is responsible for the selective deposition, which is a process widely used in microelectronics [19].

CONCLUSIONS

This study examined the applicability of the TCC in silicon hot-wire CVD. The current measurements, observation of clusters, and the bias effect on the cluster deposition behavior indicate that the films in the silicon hot-wire CVD process grow by the deposition of negatively charged clusters that nucleated in the gas phase. Crystalline films with a high mobility and a grain size of ~1 μm could be deposited on the glass substrate under the optimized deposition conditions. The highest mobility of the films was 175 cm^2/Vsec.

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REFERENCES

1. H. Matsumura. *Thin Solid Films* **395**, 1 (2001).
2. A. H. Mahan. *Thin Solid Films* **395**, 12 (2001).
3. R. E. I. Schropp. *Thin Solid Films* **395**, 17 (2001).
4. W. A. Yarbrough, R. Messier. *Science* **247**, 688 (1990).
5. N. M. Hwang, J. H. Hahn, D. Y. Yoon. *J. Cryst. Growth* **162**, 55 (1996).
6. I. D. Jeon, C. J. Park, D. Y. Kim, N. M. Hwang. *J. Cryst. Growth* **213**, 79 (2000).
7. H. S. Ahn, H. M. Park, D. Y. Kim, N. M. Hwang. *J. Cryst. Growth* **234**, 399 (2002).
8. W. S. Cheong, D. Y. Yoon, D. Y. Kim, N. M. Hwang. *J. Cryst. Growth* **218**, 27 (2000).
9. I. D. Jeon, L. Gueroudji, D. Y. Kim, N. M. Hwang. *J. Korean Ceram. Soc.* **38**, 218 (2001).
10. N. M. Hwang, D. Y. Kim. *Int. Mater. Rev.* **49**, 171 (2004).
11. D. J. Shaw. *Introduction to Colloid and Surface Chemistry*, Butterworths, London (1970).
12. P. Gerhardt, S. Loffler, K. H. Homann. *Chem. Phys. Lett.* **137**, 306 (1987).
13. K. H. Kingdon, I. Langmuir. *Phys. Rev.* **21**, 380 (1923).
14. I. Langmuir, K. H. Kingdon. *Proc. R. Soc. London, Ser. A* **107**, 61 (1925).
15. D. R. Lide. *CRC Handbook of Chemistry and Physics*, 71st ed., CRC, Boca Raton (1990–1991).
16. A. A. Howling, L. Sansonnens, L. L. Dorier, Ch. Hollenstein. *J. Phys. D: Appl. Phys.* **26**, 1003 (1993).
17. H. Matsumura. *Electrochem. Soc. Proc.* **98-22**, 280 (1998).
18. L. Liu, J. H. Edgar. *Mater. Sci. Eng. R* **37**, 61 (2002).
19. T. T. Kodas, M. J. Hampden-Smith. *The Chemistry of Metal CVD*, VCH, Weinheim (1994).