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# NO Sensing Property of Carbon Nanotube Based Thin Film Gas Sensors Prepared by Chemical Vapor Deposition Techniques

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To prepare a gas sensor that can operate at room temperature, carbon nanotubes (CNTs) were grown on $Al_2O_3$ substrates with interdigital Pt electrodes ($Al_2O_3$ substrate) by both pulsed laser deposition (PLD) and chemical vapor deposition (CVD). In this combined method, Fe catalytic thin film was prepared by PLD and then CNTs were grown on the Fe thin film by thermal CVD using an ethylene gas. The surface images of the prepared CNTs on the substrates were observed by scanning electron microscopy (SEM), and the sensitivity to NO gas was measured. The resistance of the prepared CNT-based gas sensor was found to decrease with increasing sensor temperature, and it decreased with increasing NO gas concentration at room temperature. In this paper, it is suggested that CNT gas sensors have a great possibility to be applied as innovative NO gas sensors on the basis of the experimental results. [DOI: 10.1143/JJAP.45.8393]

KEYWORDS: carbon nanotubes, PLD, thermal CVD, ethylene, gas sensor, nitrogen oxide

## 1. Introduction

In the last several years, interest in air pollutants and their monitoring has been growing. Nitrogen oxides (i.e., NO and $NO_2$) are some of the typical air pollutants that cause environmental problems. In light of these issues, it is necessary to develop highly sensitive $NO_x$ gas sensors of low cost for ambient air monitoring.

Carbon nanotubes (CNTs) are promising materials that have unique properties such as high electrical conductivity, high mechanical strength and high aspect ratio. In particular, single-walled CNTs (SWNTs) are potentially useful materials owing to their very small diameter, in addition to other properties. CNTs are expected to serve as new gas sensing materials that have an outstandingly high sensitivity at room temperature with a fast response.[1)] Several types of gas sensors using CNTs have been proposed. A gas ionization sensor, in which CNTs are used as field emission electrodes for the electrical breakdown of gas, has high levels of gas selectivity and sensitivity.[2)] Another type of CNT gas sensor is based on the change in the electrical conductance of CNTs that adsorb gas molecules.[3)] This type of sensor is expected to have a very high sensitivity and a fast response at ambient temperatures and compatibility with integrated circuits. The mechanism of SWNT gas sensors can be explained by the fact that the conductivity of the SWNTs that adsorb oxidizing gas is modified by charge transfer between the SWNT surface and the gas molecules adsorbed, as shown in Fig. 1.[4,5)]

Many methods of preparing CNTs have been reported, such as laser ablation, arc discharge, thermal chemical vapor deposition (CVD) and plasma-enhanced CVD, etc. To realize their practical applications, including their application in CNT-based gas sensors, nanotubes with desirable properties must be prepared in large quantities at a low cost. Here, we have prepared CNT thin films by thermal CVD on $Si_3N_4$ substrates and $Al_2O_3$ ceramic substrates. To prepare a sensor device, the $Al_2O_3$ ceramic substrate with a Pt interdigital electrode (hereinafter called as "$Al_2O_3$ substrate") was used. In this method, a catalytic Fe thin film was prepared by PLD and then CNTs were grown on the thin film by thermal CVD.

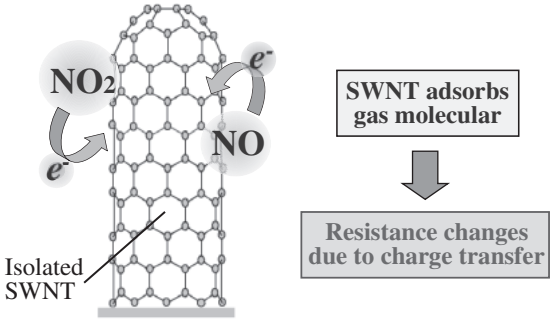


Fig. 1. Oxidation/reduction gas adsorbed on the SWNT surface changes the conductivity of the SWNT due to charge transfer between SWNT and gas molecules.

## 2. Experimental Procedure

Fe catalytic thin films were deposited on $Si_3N_4$ substrates (Si substrate covered with a $Si_3N_4$ layer) and $Al_2O_3$ substrates in a PLD system with a KrF excimer laser ($\lambda =$ 248 nm, repetition rate = 10 Hz, laser fluence = 3 J/cm$^2$), as shown in Fig. 2(a). The distance between the Fe target (purity: 99.9%) and the $Si_3N_4$ substrate or the $Al_2O_3$ substrate was set at 5 cm. The Fe thin film was deposited on the substrate at room temperature in vacuum (base pressure of $4.7 \times 10^{-3}$ Pa). The thickness and roughness of the films were varied by changing the number of ablation laser pulses: 300, 1,000, and 3,000 shots. The advantages of PLD are its simplicity of use, since the laser is completely decoupled from the chamber, and the possibility of easily producing thin films using various kinds of target materials. The thickness of the film can be controlled by the number of laser pulses. The $Si_3N_4$ substrates were used to prevent Si from forming Fe–Si silicide. The shapes of the CNTs grown on the $Al_2O_3$ substrate were similar to those of CNTs grown on the $Si_3N_4$ substrates, but the diameter of the CNTs was thinner.

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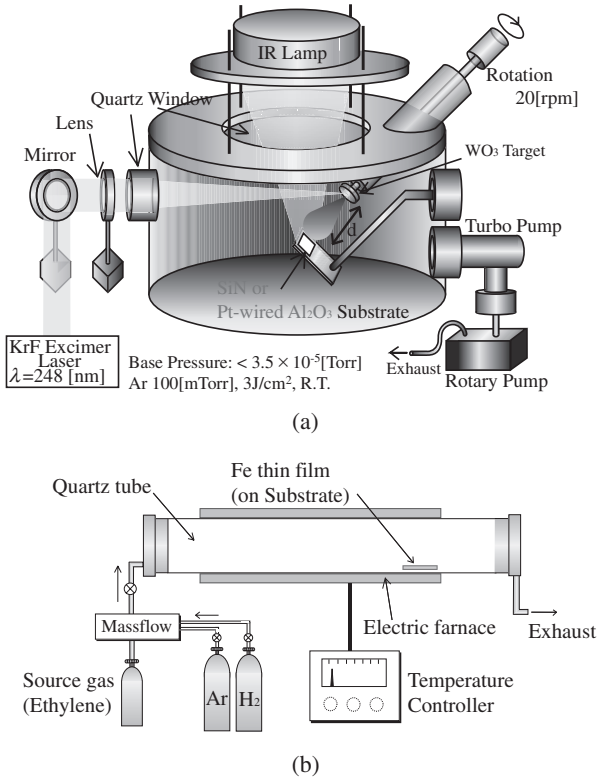



Fig. 2. Experimental apparatus of (a) PLD and (b) thermal CVD systems.

The thermal CVD system is shown in Fig. 2(b). Ethylene ($C_2H_4$) gas is diluted by Ar and/or $H_2$ gas using mass flow controllers and then made to flow into a quartz glass reaction tube, which is heated by an electric furnace up to 1000 °C. Total gas flow rate and total gas pressure are maintained at 60 sccm and 6 or 13 kPa, respectively. The Fe thin films on the $Si_3N_4$ and $Al_2O_3$ substrates prepared by PLD were set in the reaction tube and annealed in $H_2$ gas for 20 min before CNT growth. Then CNTs were grown on the substrate for 20 or 40 min in $Ar/H_2$ and $C_2H_4$ mixed gas flow. The Ar and $H_2$ gases used as buffer gas act to limit the overgrowth of CNTs. In the experiment, the gas mixture ratios of $C_2H_4 : Ar = 1 : 1$, $C_2H_4 : H_2 = 1 : 1$, and $C_2H_4 : Ar : H_2 = 1 : 1 : 1$ were examined. The Fe and CNT films were characterized using an atomic force microscope (AFM), a scanning electron microscope (SEM), and a gas sensitivity characterization system.

## 3. Results

### *3.1 Observation of Fe catalytic particle*

Figure 3 shows AFM images of the surface morphology of Fe catalytic thin film. These samples were prepared using different numbers of ablation laser pulses, (a) 3,000 and (b) 1,000 shots, and then post deposition annealed for 20 min. The mean grain sizes of the Fe thin film on the substrate are (a) 32.7 and (b) 17.8 nm. These results indicate that the mean grain size is affected by the number of laser pulse. The fewer the laser pulses, the smaller the size of Fe particles deposited. Since small catalytic particles are suitable for CNT growth,[6] 1,000 laser pulses were used for Fe film preparation. The post deposition annealing of the Fe thin film in $H_2$ ambient gas at 1000 °C seems to be effective for introducing the nucleation and activation of catalyst particles. The thickness of the Fe film prepared at 3,000 laser pulses, as obtained using by a thickness meter is about 29.4 nm. The thickness of the film for 1,000 laser pulses could not be measured using the thickness meter; however, it is estimated to be approximately of 9.8 nm as film thickness is usually proportional to the number of laser pulses in PLD. The smaller thickness of the film seems to be due to the smaller size of particles.

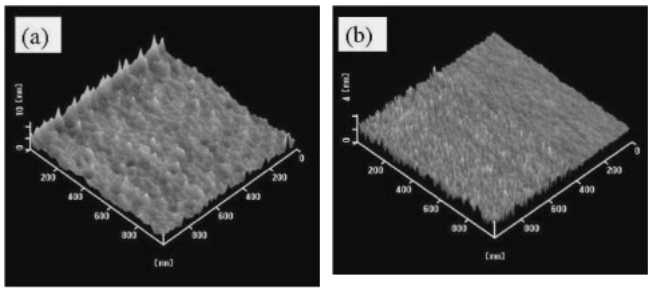



Fig. 3. AFM images of Fe thin films prepared by PLD using different number of laser pulses followed by annealing. (a) 3,000 shots. (b) 1,000 shots.

### *3.2 Observation of prepared CNTs*

SEM images of the CNTs on the $Si_3N_4$ substrates prepared using different gas mixture ratios with a growth time of 40 min and a total pressure of 13 kPa are shown in Figs. 4(a)–4(f). Hydrogen gas was used to avoid the deactivation catalytic property of the Fe thin film caused by oxidation. It was found that the number, length and thickness of produced CNTs were affected by the gas mixture ratio. In pure $C_2H_4$ gas [(a) $C_2H_4 : Ar : H_2 = 1 : 0 : 0$], CNTs were not grown on the substrate but thick carbonaceous soot or amorphous carbon was found. In Fig. 4(b), $C_2H_4 : Ar : H_2 = 1 : 0 : 1$, numerous thick CNTs (about 150 nm in diameter) were found on the substrate and a large amount of amorphous carbon was observed. In Fig. 4(c), $C_2H_4 : Ar : H_2 = 1 : 0 : 2$, thinner CNTs containing less impurity were obtained. Some CNTs had a diameter of about 50 nm. When Ar gas was used as the inert gas, in Fig. 4(d), $C_2H_4 : Ar : H_2 = 1 : 1 : 0$, a large number of long CNTs were produced, whereas in the cases of $C_2H_4 : Ar : H_2 = 1 : 2 : 0$ and $C_2H_4 : Ar : H_2 = 1 : 3 : 0$, thick CNTs and a large amount of carbonaceous matter (including amorphous carbon, SWNTs and/or MWNTs) were produced. The Ar gas ratio in the mixed gas was found to affect CNT formation.

A mixture of Ar and $H_2$ gases in Fig. 4(e), $C_2H_4 : Ar : H_2 = 1 : 1 : 1$, produced a large number of thin CNTs with less impurities. In Fig. 4(f), $C_2H_4 : Ar : H_2 = 1 : 2 : 2$, few CNTs were observed. This result seems to be due to the insufficient supply of carbon sources. From these results, it was found that $H_2$ gas tends to suppress the formation of amorphous carbon and CNTs on the substrate, whereas Ar gas tends to enhance it. From the above-mentioned results, we have found that the gas mixture ratio $C_2H_4 : Ar : H_2 = 1 : 1 : 1$ was the most suitable condition for CNT thin film preparation in our experiment.

SEM images of the prepared CNTs grown on the Fe thin film under various conditions are shown in Figs. 5(a)–5(d). In Fig. 5(a), using a shorter growth time of 20 min at

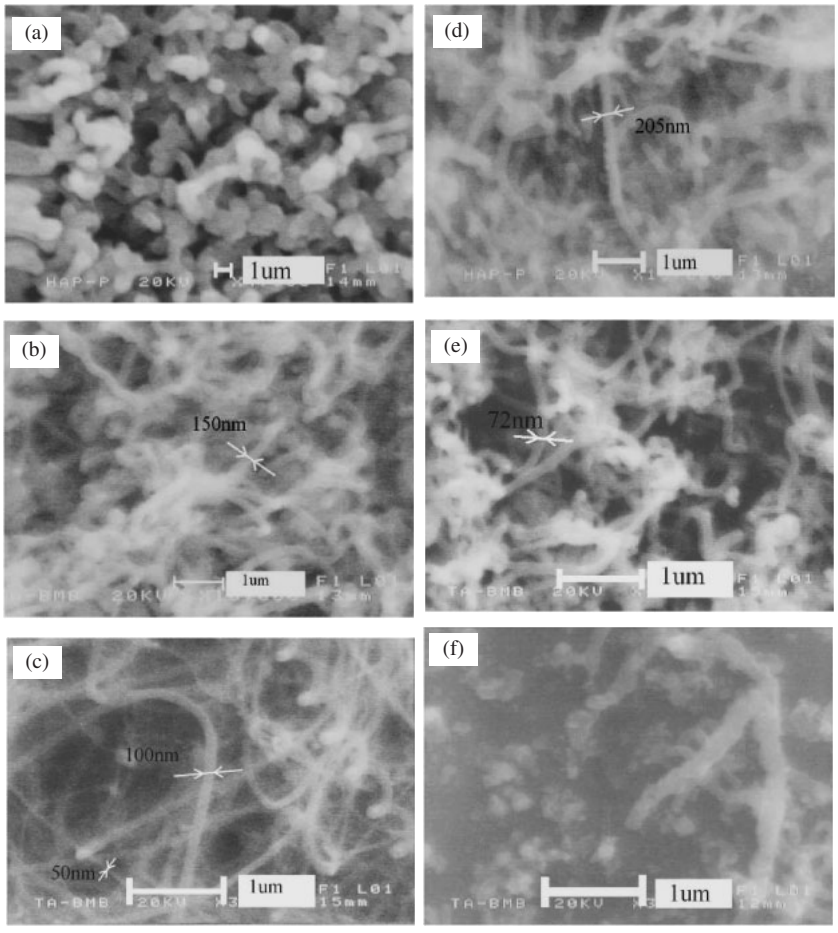



Fig. 4. SEM images of CNTs grown on Fe thin films under various gas mixture ratios (number of laser pulse is 1,000 shots at 10 Hz total gas flow rate is 60 sccm). (a) $C_2H_4 : Ar : H_2 = 1 : 0 : 0$. (b) $C_2H_4 : Ar : H_2 = 1 : 0 : 1$. (c) $C_2H_4 : Ar : H_2 = 1 : 0 : 2$. (d) $C_2H_4 : Ar : H_2 = 1 : 1 : 0$. (e) $C_2H_4 : Ar : H_2 = 1 : 1 : 1$. (f) $C_2H_4 : Ar : H_2 = 1 : 2 : 2$.

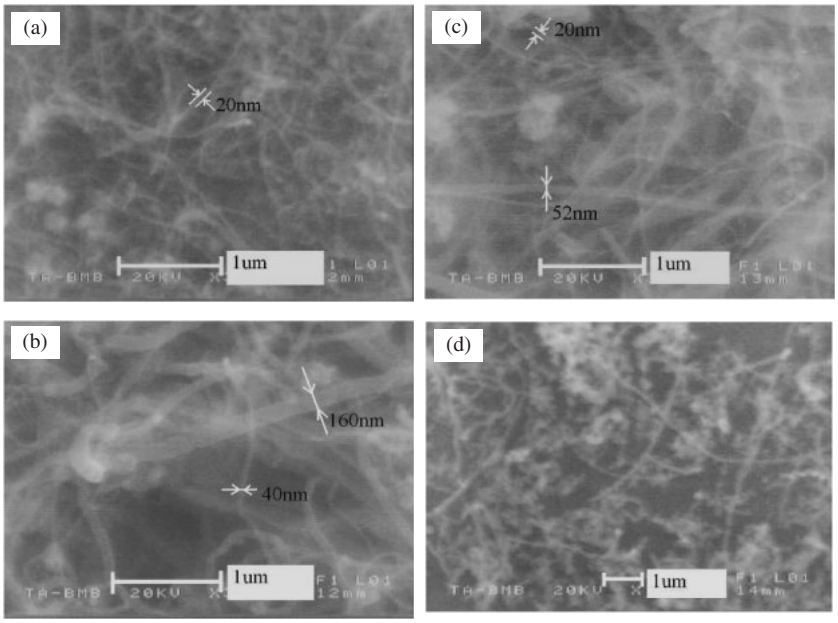



Fig. 5. SEM images of CNTs grown on Fe thin films under various condition. (a) Prepared at different deposition time. (b) and (c) Prepared at different deposition time and furnace temperature. (d) Prepared at total pressure 6 kPa. (Number of laser pulse is 1,000 shots at 10 Hz, total gas flow rate is 60 sccm. Gas mixture ratio is $C_2H_4 : Ar : H_2 = 1 : 1 : 1$.) (a) 1000 °C, 20 min, 13 kPa. (b) 800 °C, 20 min, 13 kPa. (c) 800 °C, 40 min, 13 kPa. (d) Total pressure 6 kPa, 1000 °C, 40 min.

1,000 °C [40 min in Figs. 4(a)–4(f)], thinner CNTs were prepared on the $Si_3N_4$ substrate. The diameter of the thinnest CNT in Fig. 5(a) is about 20 nm. Figures 5(b) and 5(c) show SEM images of CNTs prepared at 800 °C. The diameters of the thinnest CNTs in Figs. 5(b) and 5(c) are thinner than that of CNTs in Fig. 4(e) with $C_2H_4 : Ar : H_2 = 1 : 1 : 1$. However, in Figs. 5(b) and 5(c) show numerous carbonaceous soot particles and CNTs of different diameters. At a total pressure of 6 kPa [Fig. 5(d)], a small number of CNTs with amorphous carbon were found. CNTs were found to be dispersed on the substrate. It is considered that the diameter of a CNT is proportional to the diameter of the catalyst particle.[7,8] It appears that this dispersion in CNT diameter results in random-sized catalyst particles. It is necessary to prepare nanosized catalyst particles for the growth of the SWNTs with a uniform diameter. The thermal CVD

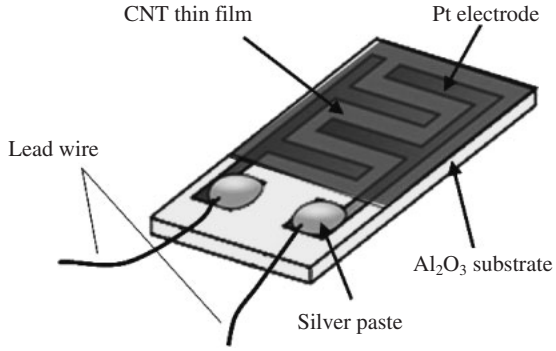



Fig. 6. Structure of sensor device. Conducting wires were fixed to tip of electrode using silver paste.

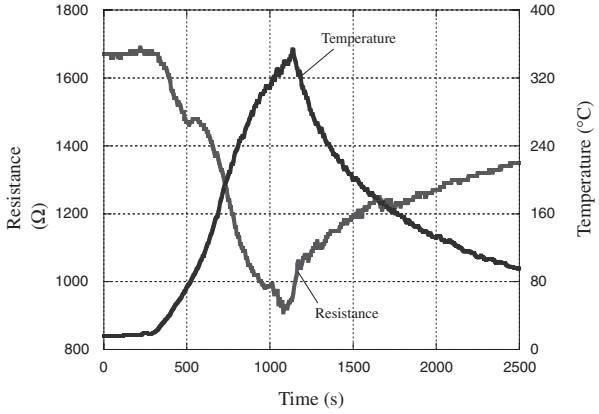
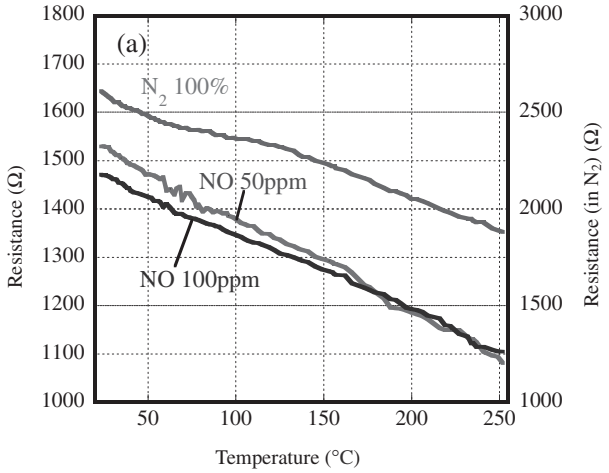



Fig. 7. Resistance of CNTs thin film gas sensor prepared at $C_2H_4 : Ar : H_2 = 1 : 1 : 1$ with 1,000 laser pulses at 10 Hz.



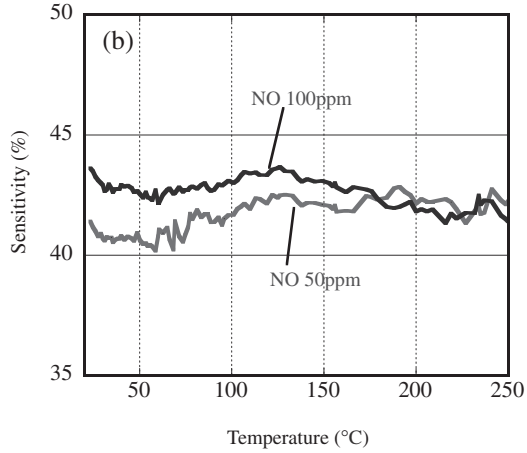




Fig. 8. Properties of CNTs thin film gas sensor prepared at $C_2H_4 : Ar : H_2 = 1 : 1 : 1$ laser pulse of 1,000 at 10 Hz. (a) Resistance–temperature characteristics of sensor in dry air, 50 and 100 NO gas. (b) Sensitivity–temperature characteristics of sensor in 40 and 100 ppm NO gas.

conditions of a furnace temperature of 1,000 °C and a growth time of 20 min [Fig. 5(a)] produced thin CNTs with relatively uniform diameters. Thus, these process conditions were used to prepare CNT thin films for the gas sensor device.

### *3.3 Gas sensing characteristic*

The properties of a CNT gas sensor in terms of sensitivity to NO gas were measured using the electrical resistance between the interdigital electrodes. The sensor shown in Fig. 6 was exposed to NO gas of different concentrations in a measurement chamber. The total pressure of the chamber was maintained at 1 atm during the measurements.

The resistance–temperature characteristics of the CNT film sensor in dry air are shown in Fig. 7. The CNT film was prepared at $C_2H_4 : Ar : H_2 = 1 : 1 : 1$, using 1,000 laser pulses and a deposition time of 20 min. The CNTs on the $Al_2O_3$ substrate were purified in a heated hydrogen peroxide water solution at 90 °C for 1 h to remove amorphous carbon. The initial resistance of the film was about 1,650 Ω and it decreased with increasing of temperature. This shows that the prepared CNT sensor film has semiconductor characteristics. The resistance–temperature characteristics of the CNT gas sensor in $N_2$ and in NO gas of 50 and 100 ppm in $N_2$ balance are shown in Fig. 8(a). The resistance of the sensor had a negative temperature coefficient and its initial resistance in $N_2$ was about 2,650 Ω. In this experiment, the CNTs sensor resistance decreased with increasing of ambient NO gas concentration. It is considered that hole density within a CNT increases owing to electron transfer between the CNT and NO molecules adsorbed at the surface of the CNT. Here, we define the sensitivity $S$ of the sensor to NO gas as follows: $S = [(R_{N_2} - R_{gas})/R_{N_2}] \times 100$ (%), where $R_{N_2}$ is the resistance in $N_2$ gas and $R_{gas}$ is the resistance in NO gas. The calculated sensitivities in 50 and 100 ppm NO as a function of temperature are shown in Fig. 8(b). The sensitivities at room temperature are found to be 44.0% in 50 ppm NO and 42.5% in 100 ppm NO gas. The sensitivity of the CNT sensor at low temperatures makes this device advantageous for practical applications. To increase sensitivity, it is necessary to increase the portion of SWNTs in the film to enlarge the specific surface area on which ambient gas molecules can attach.

## 4. Conclusions

We have successfully grown CNTs on a $Si_3N_4$ substrate by thermal CVD. AFM images show that an Fe catalytic thin film with fine grains can be prepared by PLD at laser pulses of 1,000 shots at 10 Hz. SEM images of the CNTs deposited with various gas mixture ratios show that the quantity, diameter and thickness of CNTs are affected by the ratio of the gas mixture. We found the experimental conditions of

$C_2H_4 : Ar : H_2 = 1 : 1 : 1$ and a growth period 20 min to be the most suitable conditions for preparing CNT gas sensor devices. The resistance of the prepared CNTs gas sensor decreased with increasing of ambient NO gas concentration at room temperature. The CNT gas sensors have a great potential to be applied in innovative NO gas sensors.

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