

Full Research Paper

## Synthesis and Characterization of Carbon Nitride Films for Micro Humidity Sensors

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**Abstract:** Nano-structured carbon nitride (CN<sub>x</sub>) films were synthesized by a reactive RF magnetron sputtering system with a DC bias under various deposition conditions, and their physical and electrical properties were investigated with a view to using them for micro humidity sensors. The FTIR spectra of the deposited films showed a C=N stretching band in the range of 1600~1700 cm<sup>-1</sup>, depending on the amount of nitrogen incorporation. The carbon nitride films deposited on the Si substrate had a nano-structured surface morphology with a grain size of about 20 nm, and their deposition rate was 1.5 μm/hr. The synthesized films had a high electrical resistivity in the range of 10<sup>8</sup> to 10<sup>9</sup> Ω·cm, depending on the deposition conditions. The micro humidity sensors showed a good linearity and low hysteresis between 5 ~ 95 %RH.

**Keywords:** nano-structure, carbon nitride film, humidity sensors, sputtering system

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### 1. Introduction

Carbon nitride was suspected to be exceedingly hard because of its perceived short inter-atomic distances [1]. This speculation was initiated by Liu and Cohen in 1989 [2] based on an empirical model and *ab initio* calculation of the bulk modulus for covalent solids formed between carbon and nitrogen. They reported that if the crystalline β-C<sub>3</sub>N phase, whose structure was similar to that of β-Si<sub>3</sub>N<sub>4</sub>, could be synthesized, its hardness and heat conductivity would be comparable with or even superior to that of diamond. Unfortunately, attempts to synthesize the exact stoichiometric β-C<sub>3</sub>N<sub>4</sub> phase have so far been unsuccessful. Nevertheless, many reports have been published on the use of amorphous carbon nitride (a-CN<sub>x</sub>), mostly produced by reactive sputtering [3, 4], laser ablation [5] and

CVD [6], as a protective material on hard disks and read heads [7, 8], photoluminescence [9-11], carbon nitride nanotubes [12, 13], and gas sensors having an  $a\text{-CN}_x\text{:H}$  structure [14].

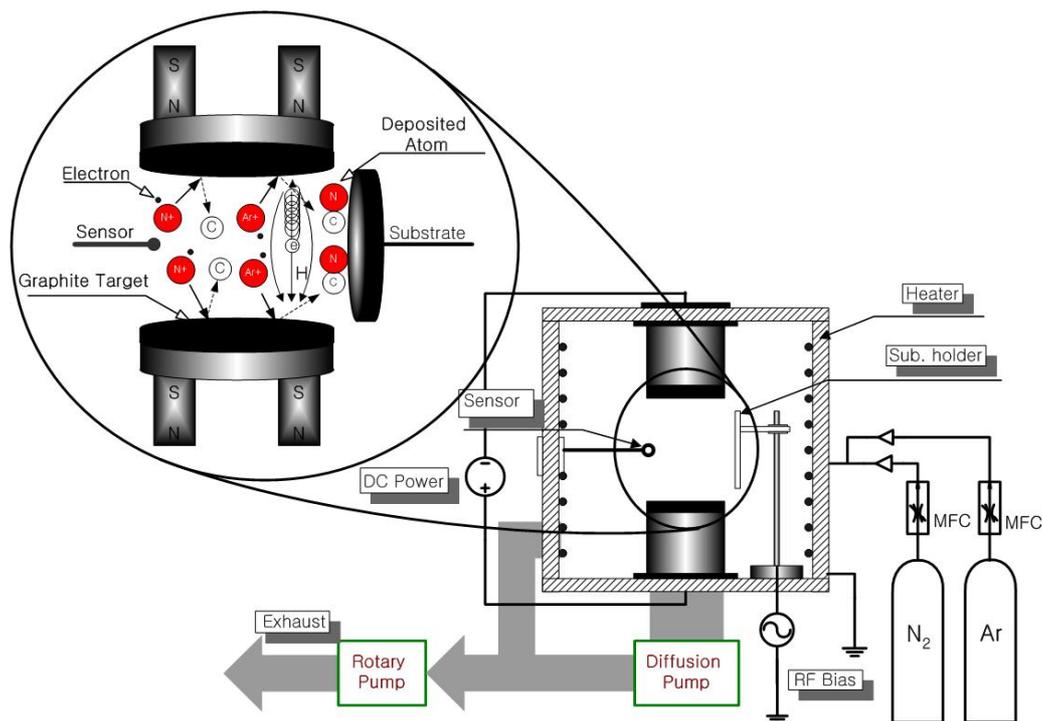
One of the most significant obstacles to the synthesis of crystalline  $\beta\text{-C}_3\text{N}_4$  is the existence of N-H and C-H bonds which are formed in most sputtering systems. However, it was suggested that the undesired effect caused by the reaction with hydroxyl group of carbon nitride films by a hydrogen attack could be applied to humidity sensors [4]. The hydrogen attack to carbon nitride film could easily break or change the  $\text{C}\equiv\text{N}$  and  $\text{C}=\text{N}$  bonds to form C-H and N-H bonds. This behavior is strongly undesirable from the viewpoint of obtaining crystalline  $\beta\text{-C}_3\text{N}_4$ . However, if one could make use of hydrogen defects which were formed intentionally and bonded weakly, carbon nitride would be an attractive candidate material for humidity sensor applications.

Semiconductor micro sensors, in which semiconductor materials are chiefly responsible for the sensor operation, are a worthwhile subject to be investigated in terms of the development of miniaturized and high performance sensors. Humidity sensors, a type of chemical sensors, are used in a wide range of applications, from general home and office application to industry fields, hospitals and laboratories that need greater accuracy and strict conditions. Commercial humidity sensors are generally made of polymers with a dip-coating method. However, although this technique is inexpensive and facile, it is difficult to make micro sensors on a semiconductor substrate (usually silicon) that operates at relatively high temperature. Therefore, for the development of micro- or on-chip sensor, not only good humidity sensing but also flexible properties are required.

In this paper, we report the physical and electrical properties of carbon nitride films deposited by a reactive rf magnetron sputtering system with dc bias, and the possibility of using them as new humidity sensing materials for micro humidity sensors.

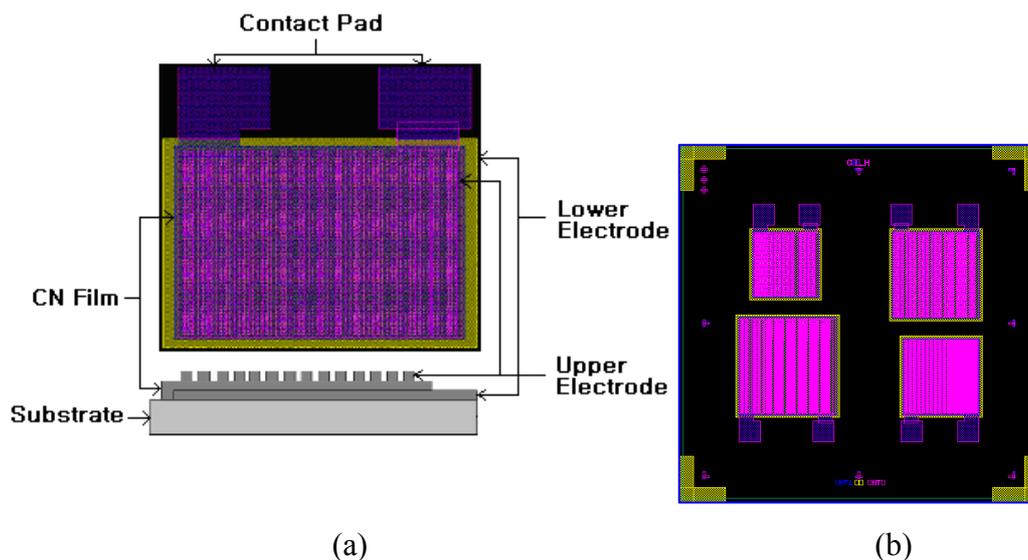
## 2. Experimental

The carbon nitride film was formed by the reaction of nitrogen gas (99.999 %) with a 3 inch carbon target (99.99 %) in the facing target sputtering chamber. The ratio of nitrogen to argon, controlled by mass flow controller (MFC), was 7:3, which was reported in a previous work to be the condition allowing for the highest amount of nitrogen to be incorporated [3]. To reduce the influence of contamination from the chamber wall and undesirable gases, the whole chamber wall was heated, and a thermocouple was attached to the back of the substrate holder, in order to maintain the substrate temperature precisely at 150 °C. Fig. 1 shows a schematic of the reactive RF magnetron sputtering system with dc bias. SEM (ABT-32, TOPCON) was used to observe the surface morphology of the films. The FTIR spectra were obtained by Research I series Mattson with  $4\text{ cm}^{-1}$  resolution. Film thickness was determined by Alpha-Step 500 (KLA-Tencor), and TGA/DTA study was made with SDT2960 (TA instruments).



**Figure 1.** A schematic diagram of facing target RF magnetron sputtering system.

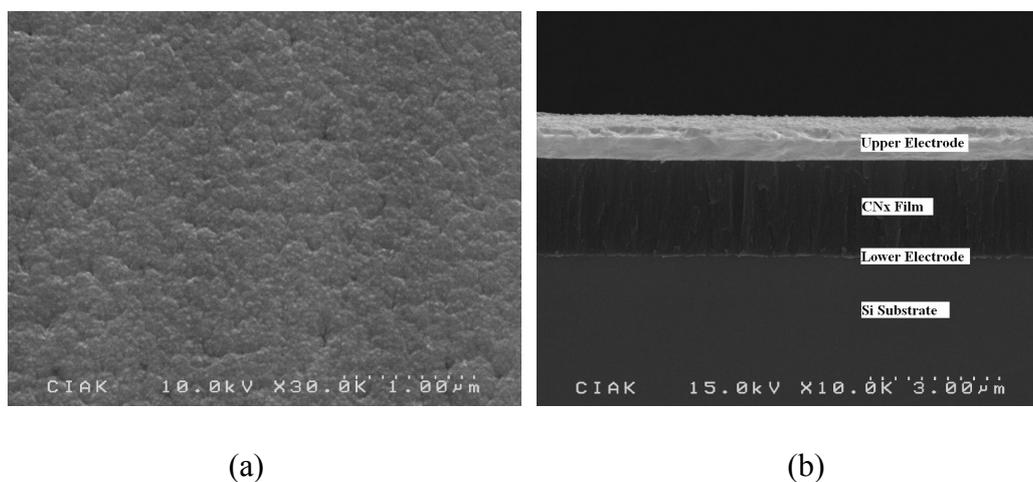
The humidity sensor was designed as a capacitive type with square meshed windows ( $5 \mu\text{m} \times 5 \mu\text{m}$ ) to enhance the absorption and the desorption response of the sensing materials. An Al upper electrode was deposited on the carbon nitride film by the lift-off technique. A schematic view of the capacitive type humidity sensor is illustrated in Fig. 2. To show the influence of water vapor on the  $\text{CN}_x$  film, a humidified film was prepared in a water saturated chamber. MFCs were used to control the humidity in the measuring chamber by regulating the flow rates of dry air and vapor-saturated air. To avoid the condensation of water vapor on the inner walls of the chamber or pipelines, caused by the difference in temperature between the incoming vapor and the inside of the chamber, all measurement objects were put together in a constant-temperature box controlled by PID controller [4]. A special self-made measurement chamber having 25 mm thick duralumin walls was used to obtain precise humidity measurements without any external gas inflow or electrical noises. The chamber size was 270 mm in width, 440 mm in length, and 160 mm in height. It also had a gas inlet and outlet, ten BNC connectors, and two 9 pin D-SUB connectors and a pressure gauge on the front panel. The outlet was connected to a small vacuum pump for rapid evacuation. In the chamber, four manipulators were installed for the purpose of probing small size devices. A commercial temperature-humidity sensor was also included to measure the reference temperature. The cover had a quartz window at the center for observing inside the chamber and a stereomicroscope was installed above the window.



**Figure 2.** A capacitive type humidity sensor with meshed top electrode; (a) schematic view and (b) mask layout.

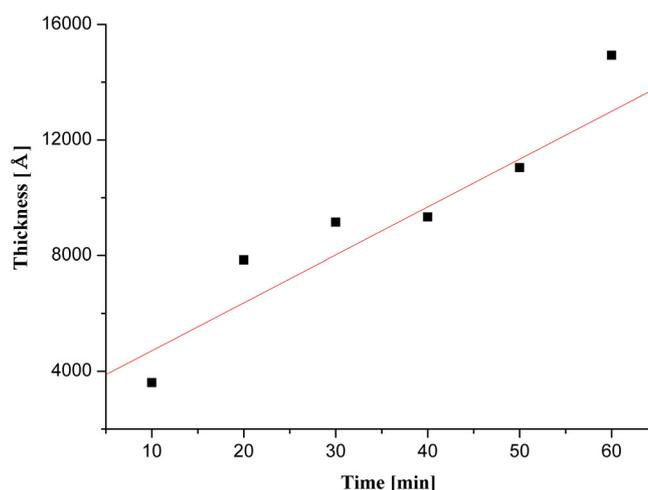
### 3. Results and Discussion

Fig. 3 shows the SEM images of the Al/CN<sub>x</sub>/Al/Si structure, in which the carbon nitride film was formed with an RF power of 200 W for 1hr. The growth rate of the film is about 1.5 μm/hr. The film is composed of nano-structured grains (ca. 20 ~ 40 nm), which have a dense morphology, as shown in Fig. 3(a). The lower electrode is thinner than the upper electrode in Fig. 3(b), because Ar sputtering was performed in order to remove the contaminant on the lower electrode surface before the deposition of the CN<sub>x</sub> film. Furthermore, Al from the lower electrode diffused into the Si substrate forming aluminum silicide.



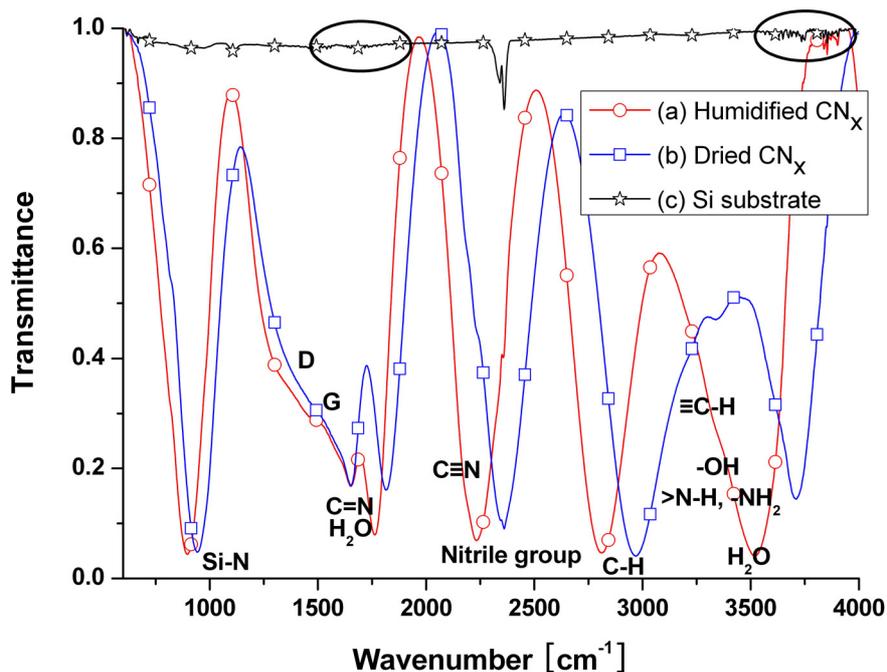
**Figure 3.** SEM images of CN<sub>x</sub> film deposited on Si-wafer; (a) surface and (b) cross section.

A uniform growth rate is one of the most important factors in the carbon nitride deposition process. The film thickness determines the sensor performance in the case of both resistive and capacitive type sensors. Yu et al. [15] first produced non continuous crystalline  $\beta$ - $C_3N_4$  films by the diode sputtering technique. The substrates were in contact with the plasma and were therefore subjected to bombardment by the plasma electrons and ions as well as by the energetic primary electrons. They said that this electron bombardment effects not only causes a higher substrate temperature, but also has an effect on the film growth. Films prepared by this method were completely amorphous and had a nonlinear growth rate. Thus, it is necessary to have a sputtering system in which electrons can be completely trapped, in order to rule out the effect of electron bombardment. These trapped electrons cause a higher degree of ionization and this can be one of the key factors allowing for the deposition of crystalline carbon nitride. Fig. 4 illustrates the relationship between the thickness of the  $CN_x$  film and the deposition time. The film thickness is proportional to the deposition time, because DC bias of the substrate provides control over the electrons, and the heating of the whole chamber reduces the effect of the higher substrate temperature due to electron bombardment. From the fitting line, the growth rate is about 1.5  $\mu\text{m/hr}$ .



**Figure 4.** Relation between the thickness of the  $CN_x$  films and deposition time.

To determine the influence of the adsorption of water vapor, two samples were prepared for FTIR analysis, viz. the humidified  $CN_x$  film kept in the chamber at over 90 %RH for 24 hr and the dried sample kept in the dehydrated chamber purged with  $N_2$  for 24 hr. The spectra of the humidified  $CN_x$  film (Fig. 5(a)) and the dried  $CN_x$  film (Fig. 5(b)) both have Si-N ( $940\text{ cm}^{-1}$ ), D ( $1270\text{-}1410\text{ cm}^{-1}$ ), G ( $1520\text{-}1590\text{ cm}^{-1}$ ), C=N ( $1600\text{-}1700\text{ cm}^{-1}$ ),  $C\equiv N$  ( $2200\text{ cm}^{-1}$ ), nitrile group ( $2367\text{ cm}^{-1}$ ) and C-H ( $2970\text{ cm}^{-1}$ ) peaks. However, some peaks, such as  $\equiv\text{C-H}$  ( $3300\text{ cm}^{-1}$ ), -OH ( $3400\text{ cm}^{-1}$ ),  $>\text{N-H}$  and  $-\text{NH}_2$  ( $3200\text{ - }3380\text{ cm}^{-1}$ ) and  $\text{H}_2\text{O}$  ( $3500\text{ cm}^{-1}$ ), are dominant in the humidified  $CN_x$  films, and are remarkably reduced in the dried  $CN_x$  films. This demonstrates that the  $CN_x$  film reacts easily with hydrogen and/or hydroxyl groups. The peak shift due to the adsorption of water vapor is clearly observed. The spectrum of the Si substrate (Fig. 5(c)) is included as a reference.

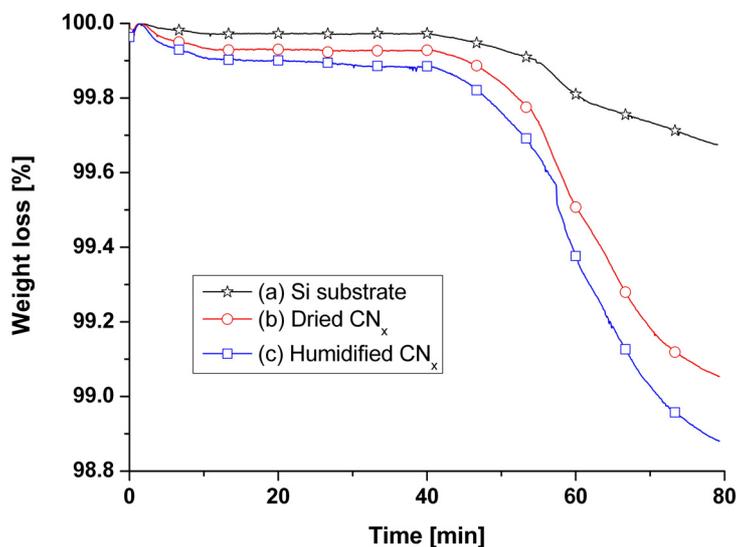


**Figure 5.** FTIR spectra of humidified  $\text{CN}_x$  films (a), dried  $\text{CN}_x$  films (b), and Si substrate (c) for the reference.

The perfect carbon nitride,  $\beta\text{-C}_3\text{N}_4$  or  $\alpha\text{-C}_3\text{N}_4$ , has been considered as an extremely stable material, which rarely react with any other gas or chemical in the room temperature. Unstable carbon nitride films, however, react with hydrogen in the air, and then  $\text{C}\equiv\text{N}$  or  $\text{C}=\text{N}$  bonds break and they change into C-H and N-H bond [4]. It can be assumed that the reaction of hydroxyl group with carbon nitride would be similar to the reaction of hydrogen. The  $\text{C}\equiv\text{N}$  bonding breaks up and the released nitrogen and carbon form C-HO and N-HO bonding. The C-HO bond starts to form at the surface due to presence of excess carbon. In the case of paracyanogen ( $\text{C}=\text{N}$ ), carbon atom can accommodate two hydrogen atoms to become stabilized. In addition, C-H and N-H bonds formed in advance can return  $\text{C}\equiv\text{N}$  and/or  $\text{C}=\text{N}$  bonds when in case of dry atmosphere. Therefore, hydrogen-defected carbon nitride films can provide dangling sites to capture water molecular physically or chemically. This can enhance the humidity sensing property of carbon nitride films. If the film surface has more defects, this can offer more adsorption sites to water vapor. Therefore, the impedance of the  $\text{CN}_x$  films would be expected to be dependent on the relative humidity, thus making them a candidate material for humidity sensors. When the carbon atoms are in the tensile stretching condition, the next layers of nitrogen atoms in the ring undergo compressive stretching to make the chain stable, and this compression becomes highly supportive when hydrogen and/or  $\text{OH}^-$  groups are present in the ambient.

Fig. 6 shows the TGA curves of the Si substrate, the dried  $\text{CN}_x$  film and the humidified  $\text{CN}_x$  film. Temperature was raised from 20 °C to 200 °C at a rate of 20 °C/min, held at this temperature for 30 min to reduce the errors due to water desorption, and then raised to 1,000 °C at 20 °C/min. After the initial 10 min at 200 °C, most of the physically adsorbed water molecules are desorbed. The Si substrate (Fig. 6(a)), dried  $\text{CN}_x$  film (Fig. 6(b)) and humidified  $\text{CN}_x$  film (Fig. 6(c)) lost 0.0037%, 0.037% and 0.057% of their weight after 10 min at 200 °C, respectively. The dried and humidified film lost 0.8742 % and 1.002% of their weight of in the temperature range of 200 °C to 1000 °C,

respectively. The physical adsorption of water takes place very rapidly on the solid surface. However, its desorption sometimes occurs slowly due to gaseous diffusion in porous adsorbents. The fact that the humidified sample loses more weight than the dried sample in the temperature range over 200 °C demonstrates that the CN<sub>x</sub> film has some pores.

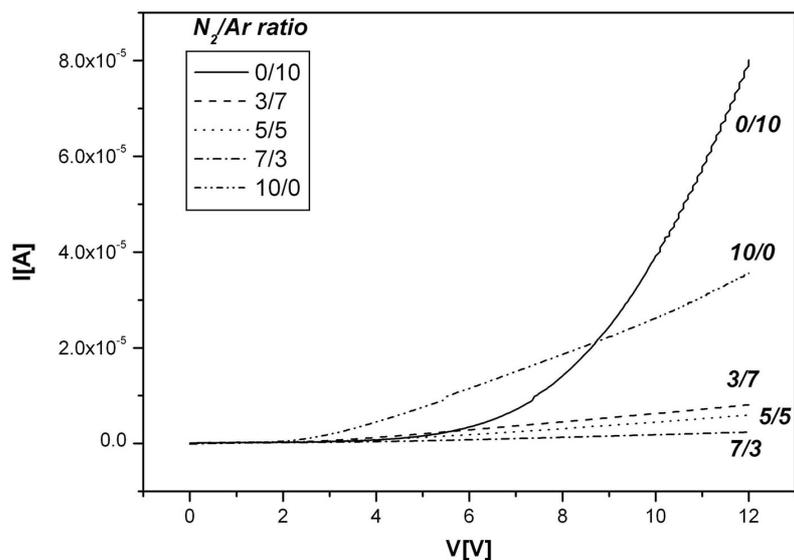


**Figure 6.** Weight loss curves of Si substrate (a), dried CN<sub>x</sub> film (b) and humidified CN<sub>x</sub> film (c).

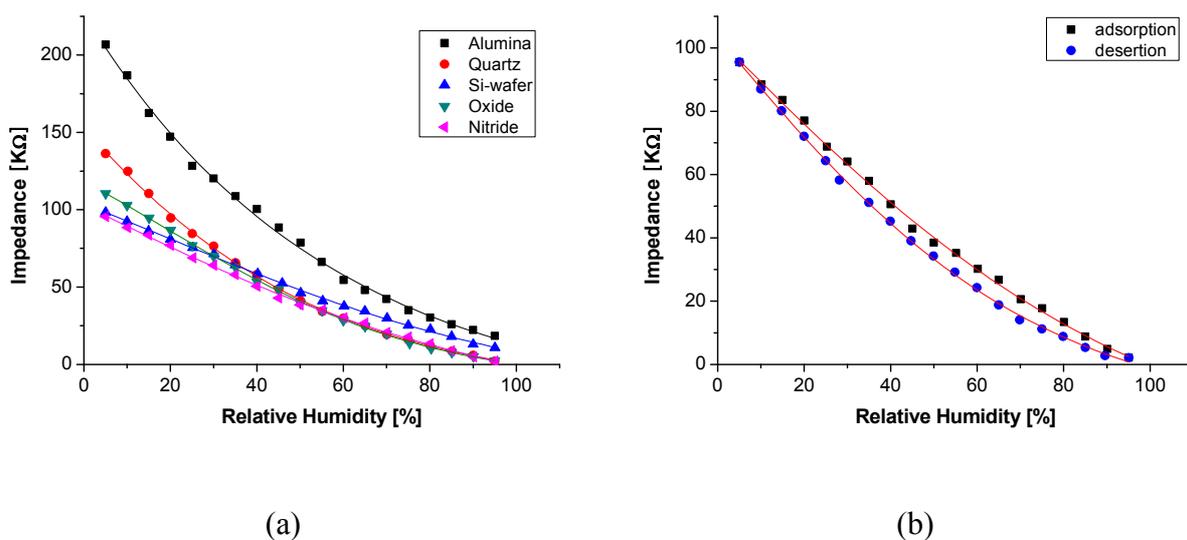
The current transport in a CN<sub>x</sub> film-semiconductor junction is due to mainly to majority carriers as opposed to minority carriers in the semiconductor-semiconductor junction. The current-voltage characteristics of the CN<sub>x</sub> films deposited at different N<sub>2</sub>/Ar ratio are shown in Fig. 7. When only Ar is used as the sputtering gas, a semiconducting carbon film can be formed, in which case the current-voltage curve is similar to that of a typical p-n junction, though the built-in potential (6.3 V) is higher than that of a Si pn junction. However, the CN<sub>x</sub> films are characterized by a higher electrical resistivity of more than 10<sup>8</sup> Ω·cm, depending on the deposition conditions. The resistivity increases from 2.42×10<sup>8</sup> to 4.46×10<sup>9</sup> Ω·cm as the nitrogen fraction increases from 0 to 70 %. This has also been reported by other research groups [16].

When more water vapor is adsorbed on the CN<sub>x</sub> film surface, the water molecules will cluster to form a liquid-like multilayer consisting of hydrogen-bonded water molecules; the formation of the multilayer due to the presence of abundant physically adsorbed water can be confirmed by the increase in the dielectric constant. Since the hydration of H<sub>2</sub>O and H<sup>+</sup> into H<sub>3</sub>O<sup>+</sup> is energetically favorable in liquid water, the dominant charge carrier in an atmosphere with high moisture content is H<sup>+</sup>. The concentration of H<sup>+</sup> increases with increasing water vapor content, then H<sup>+</sup> can move freely in liquid water, the result being a decrease of the grain resistance with increasing relative humidity [4]. Fig. 8 shows the impedance characteristics in the adsorption process of the carbon nitride humidity sensors deposited on different substrates, such as alumina, quartz, Si wafer, SiO<sub>2</sub>/Si and Si<sub>3</sub>N<sub>4</sub>/Si. The film deposited on the alumina substrate (Fig. 8(a)) shows the highest variation in impedance with the relative humidity. This impedance change is caused by the increase in the number of adsorption site due to the roughness of the substrate surface, which provides more interaction areas between the film and water molecules. The impedance change of the film deposited on the silicon-based substrate is relatively small, however, its linearity is better than that of the others. The impedance of carbon nitride

film on the  $\text{Si}_3\text{N}_4/\text{Si}$  substrate changed from 95.53 to 2.15  $\text{k}\Omega$  in the relative humidity range of 5 to 95% at 25°C. Even though the impedance changes of the films deposited on alumina and quartz have a wider span, their hysteresis is larger than that of the film deposited on the silicon-based substrate as shown in table 1. The hysteresis of humidity sensors is caused by ink-bottle shaped pores that are wider in the interior than at the surface [17]. The condensed water vapor in the pores cannot easily come out. We can see that the film deposited on alumina has a much greater number of ink-bottle shaped pores because of its high roughness. The hysteresis of the films deposited on the  $\text{Si}_3\text{N}_4/\text{Si}$  is about 4.2 %-FSO at 50 %RH. The film has a low surface roughness, so that the adsorbed water molecular can be easily desorbed.



**Figure 7.** Current-voltage characteristics of carbon nitride films as a function of  $\text{N}_2/\text{Ar}$  ratio.

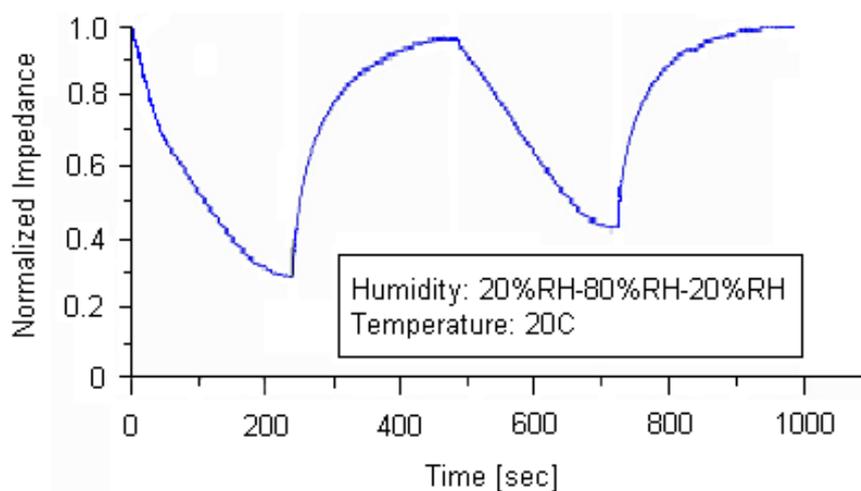


**Figure 8.** Impedance changes to relative humidity of carbon nitride films at 25 °C; (a) with different substrates, and (b) hysteresis in the silicon nitride substrate.

**Table 1.** Impedance variation, hysteresis and surface roughness of carbon nitride films with different substrates.

Substrate	Impedance changes (K $\Omega$ ) (5%RH – 95%RH)	Hysteresis (FSO, %)	Surface roughness (nm)
Alumina	188.27	17.03	308.6
Quartz	134.16	12.5	4.566
Silicon wafer	87.56	7.95	2.895
SiO <sub>2</sub> /Si	108.12	3	4.562
Si <sub>3</sub> N <sub>4</sub> /Si	93.38	4.16	3.358

To get the time response and the reversibility characteristics of the sensors, two different humidity columns of 80 %RH and 20 % RH are prepared in a measuring chamber. A sensor is moved automatically from one column to the other column by PID controller. Fig. 9 shows the response curve of the carbon nitride sensor with silicon substrate, in which the impedance is normalized. The response time is defined as the interval time between 10 % and 90 % of its full range. Adsorption and desorption time according to the column transit change are about 150 sec and 175 sec, respectively. Like most other chemical sensors, desorption time is longer than adsorption time.



**Figure 9.** Response characteristics of the carbon nitride humidity sensor with Si substrate.

#### 4. Conclusions

Carbon nitride film was formed by the reaction of nitrogen gas and a carbon target for use in capacitive type humidity sensors with micro windows (5  $\mu\text{m}$   $\times$  5  $\mu\text{m}$ ). The deposited film has nano-structured grains (ca. 20 ~ 40 nm) and its growth rate is about 1.5  $\mu\text{m}/\text{hr}$ . The CN<sub>x</sub> films have high electrical resistivities of over 10<sup>8</sup>  $\Omega\cdot\text{cm}$ . The resistivity increases from 2.42 $\times$ 10<sup>8</sup> to 4.46 $\times$ 10<sup>9</sup>  $\Omega\cdot\text{cm}$ , as the nitrogen fraction increases from 0 to 70 %. The CN<sub>x</sub> films adsorb water vapor and the adsorbed

water molecules can be easily changed to C-H and N-H bonds. The weight loss of the humidified  $CN_x$  film is greater than that of the dried film. The film which was deposited on the  $Si_3N_4/Si$  substrate with 70 %  $N_2$ , shows good linearity over a wide ranges of humidity (5 ~ 95 %RH) and shows a low hysteresis about 4.2 % FSO at 50 %RH. The  $CN_x$  humidity sensors deposited on the silicon based substrate show high linearity and small hysteresis characteristics.

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