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# Applications of Carbon Materials for Ferroelectric and Related Materials

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## 1. Introduction

Ferroelectricity is spontaneous electric polarization of a material without an external electric field and the polarization can be reversed by applying an external electric field as shown in Fig.1 (Känzig, 1957; Lines & Glass, 1979). Because the spontaneous polarization of the material is changed by an external stimulus, ferroelectric materials are also piezoelectric and pyroelectric, when the stimuli are force and heat, respectively. Ferroelectric materials have non-linear polarization; thus, they can be used as capacitors with tunable capacitance. Moreover, the hysteresis effect of the spontaneous polarization of ferroelectric materials enables the application of ferroelectric random-access memories (RAMS) for computers and radio-frequency identification (RFID) cards (Buck, 1952). In addition, piezoelectric materials are used for high voltage power source, sensors, and actuators. In these systems, it is evident that ferroelectric and related materials are not used alone. For complete systems, other materials are required to compensate for the poor properties, such as the low conductivity of piezoelectric concrete, or to enhance their performance (Shifeng, 2009; Ishiwara 2009).

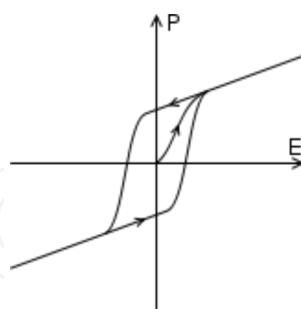


Fig. 1. The unique spontaneous polarization of ferroelectric materials

Carbon materials are used extensively in various forms in a variety of systems, because of their high thermal and chemical stability, and excellent mechanical, electrical, and electrochemical properties, which can be maximized by using an appropriate process. The various useful properties of carbon materials are attributed to their unique structures as shown in Fig.2 (Wei et al., 1993; Cousins, 2003; Frondel & Marvin, 1967; Kroto et al., 1985; Wang et al., 2009). Diamonds are famous for their impressive mechanical properties, which result from the strong covalent bonds based on  $sp^3$  hybridization only between carbon atoms. On the other hand, carbon materials, such as fullerenes and carbon nanotubes

(CNTs), have excellent electrical or electrochemical properties, such as low resistance, due to the  $\pi$ - $\pi$  conjugations based on  $sp^2$  hybridization. Of the abovementioned carbon materials  $sp^2$  carbon materials are attractive for use with ferroelectric and related materials, due to their excellent electrical properties, such as good conductivity and low resistance. Therefore, this chapter introduces carbon materials, with their unique and excellent properties, for applications in ferroelectric and related materials.

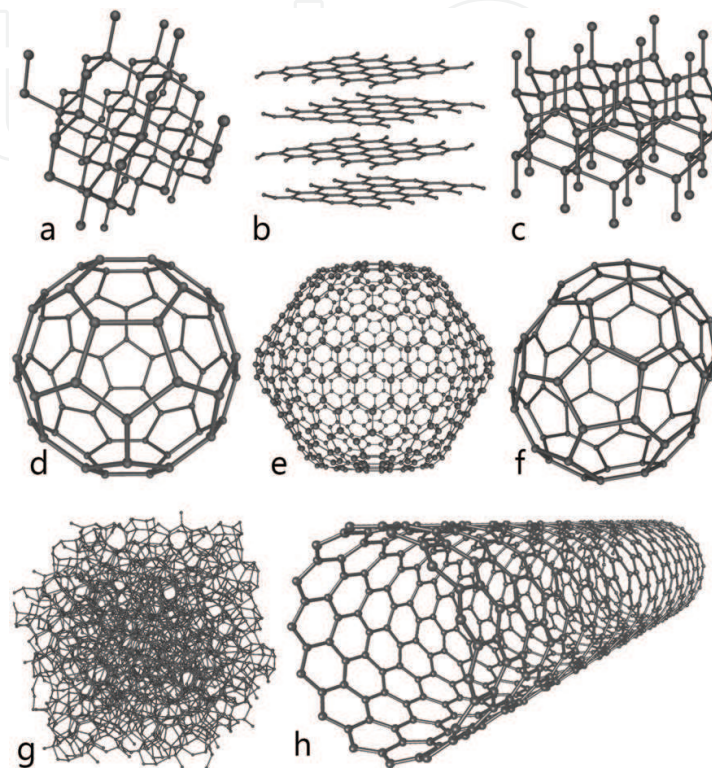


Fig. 2. Carbon materials in various multi-atomic structures with different chemical configurations: (a) diamond, (b) graphite, (c) lonsdaleite, (d) C60, (e) C540, (f) C70, (g) amorphous carbon, and (h) single-walled carbon nanotube

## 2. Ferroelectric materials assisted by carbon materials

Ferroelectric random access memory (FeRAM) has been considered for non-volatile memories, because it has the lowest power consumption among various semiconductor memories and its operation speed is similar to that of dynamic RAM (DRAM) (Arimoto & Ishiwara, 2004). A single ferroelectric-gate FET (field effect transistor) is the main component of FeRAM. However, fabricating ferroelectric-gate FETs with excellent electrical properties is difficult, due to the diffusion problem. When a ferroelectric material, such as lead zirconate titanate (PZT), is deposited directly on a Si substrate, forming a film, the constituent element of the substrate and film are diffused, or mixed, during the crystallization process. One way to avoid this diffusion problem is to insert an insulating buffer layer between the Si substrate and a ferroelectric film. Fig.3. shows the resulting gate structure, either an MFIS (Fig.3(a)) or MFMIS (Fig.3(b)) structure (M: metal, F: ferroelectrics, I: insulator, and S: semiconductor) (Ishiwara, 2009). However, inserting the buffer layer raises new problems, such as short data retention time and high operation voltage. Using CNT is one of the efficient methods for solving these problems.

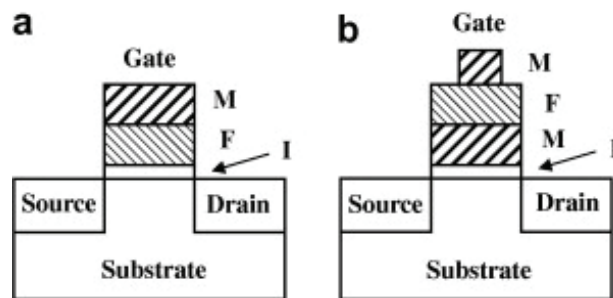


Fig. 3. Schematic drawings of (a) MFIS and (b) MFMIS gate structures (Ishiwara, 2009)

Whereas an insulating buffer layer is usually inserted between a Si substrate and the ferroelectric film in a ferroelectric-gate Si transistor, direct contact between the substrate and the ferroelectric film (MFS structure) can be achieved in a ferroelectric-gate CNT transistor (Fig.4.), due to the absence of dangling bonds on the surface of ideal CNTs. The direct contact in a ferroelectric-gate FET is expected to achieve longer data retention time with a lower operation voltage than that in a FET with MFIS gate structure, because no depolarization field is generated in the ferroelectric film. In addition, the high current drivability of CNTs also enables ferroelectric-gate CNT transistors to be one of the most promising candidates for future high-density non-volatile memories.

The current through a CNT in CNT transistors comes from thermally assisted tunneling through the source Schottky barrier J. Appenzeller, M. Radosavljevic, J. Knoch and Ph. Avouris, *Phys. Rev. Lett.* 92 (2004), p. 048301. (Appenzeller et al., 2004). Thus, the gate voltage lowers the Schottky barrier height and produces a high electric field at the semiconductor surface, rather than modulating the channel conductance. In addition, in the MFS structure, no depolarization field is expected to be generated in the ferroelectric film with zero external voltage. Thus, zero electric field exists for both directions of the remnant polarization. As a result, the polarization direction in the ferroelectric film is hard to be read out by drain current in a FET with drain electrodes and a Schottky barrier source. Therefore, it is easier to discuss the operation characteristics of ferroelectric-gate CNT transistors, semi-quantitatively.

A simplified current modulation model at the source Schottky barrier in a Si transistor can be applied to a ferroelectric-gate CNT after changing the dielectric gate insulator to a ferroelectric (Tsutsui & Asada, 2002). Fig.5 is a one-dimensional energy band diagram at the source edge in a ferroelectric-gate FET and it assumes that the work functions of the gate and source metals are the same. Because a CNT transistor has a very thin semiconductor thickness as shown in Fig.5, the semiconductor can be assumed to be an insulator, when the doping density of the CNT is not very high. This assumption enables the source region in the ferroelectric-gate FET to be expressed as an MFIM structure, which is indicated in the dotted square of Fig.4. In an MFIM structure, the first M is the gate metal, F is a ferroelectric, I is a CNT, and the last M is the source metal. A graphical method can be used in this one-dimensional structure to calculate electric fields in both F and I films easily (Ishiwara, 2001). Interestingly, the depolarization field appears even in a CNT transistor with MFS gate structure.

The average electric field in the semiconductor can be calculated under the assumption that relative dielectric constant of the semiconductor is the same as that of Si (11.8) and the ferroelectric film has the remnant polarization of  $3 \mu\text{C}/\text{cm}^2$  and a square-shaped P-V hysteresis. Moreover, the calculated average electric field in the semiconductor is  $3 \text{ MV}/\text{cm}$ ,

which is independent of the semiconductor thickness. Because the calculated value is much higher than the dielectric breakdown field of Si, which is less than 1MV/cm, sufficient charge can be injected into the semiconductor when the electric field lowers the Schottky barrier height. However, the depolarization field in the ferroelectric film is not high, which can be explained by the diagram as shown in Fig.5. The product of film thickness and electric field, which is the voltage across the film, was the same between the ferroelectric and semiconductor films under the zero bias condition. Moreover, holes were injected after the application of negative gate voltage, whereas no holes were injected after the application of a positive gate voltage. Combining this charge injection model with the voltage drop model at the drain Schottky barrier (Tsutsui, 2002) produced  $I_D-V_D$  characteristics of a ferroelectric-gate CNT FET.

Ishiwara reported two structures, CNTs deposited with SiO<sub>2</sub>/Si and SBT/Pt/Ti/SiO<sub>2</sub>/Si structures using a spin-coated method. In the CNTs deposited with SiO<sub>2</sub>/Si structure, Si substrate is used as the gate electrode in the MOS-CNT transistors, whereas a Pt film is used in the CNTs deposited with SBT/Pt/Ti/SiO<sub>2</sub>/Si ferroelectric-gate FETs. However, both transistors had charge injection-type hysteresis loops. Therefore, the first step for realizing ferroelectric-gate CNT transistors is elimination of the spurious hysteresis loops.

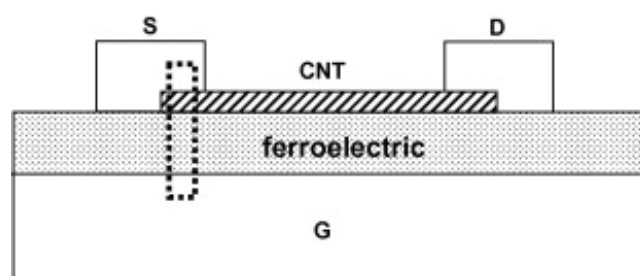


Fig. 4. Schematic drawing of a ferroelectric-gate CNT transistor (Ishiwara, 2009)

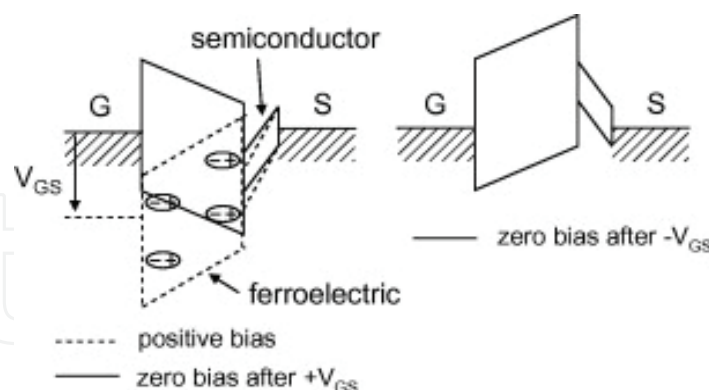


Fig. 5. One-dimensional energy band diagram at the source edge in a ferroelectric-gate Schottky FET (Ishiwara, 2009)

### 3. Piezoelectric materials assisted by carbon composites

Cement-based piezoelectric composites have been studied for applications, such as sensors and actuators in civil engineering (Li et al., 2002; Cheng et al., 2004; Chaipanich et al., 2007). These sensors and actuators have a great potential to be used for non-destructive performance monitoring of bridges and dams, for example (Sun et al., 2000). The



piezoelectric composites have been prepared with a variety of different connectivity patterns, and the 0-3 connectivity is the simplest (Newnham et al., 1978). In a 0-3 cement-based piezoelectric composite, a three-dimensionally connected cement was loaded with a zero-dimensionally connected active piezoelectric ceramic particles. PZT is mainly used for piezoelectric ceramic and has high dielectric constant and density, which results good piezoelectric properties. The 0-3 cement-based piezoelectric composite is also compatible with concrete, the most popular host material in civil engineering. In addition, cement-based composites are easy to manufacture and amenable to mass production (Li et al., 2002; Huang et al., 2004; Cheng et al., 2005). However, the 0-3 cement-based piezoelectric composites are complicated by poling because the ceramic structure does not form a continuously connected structure across the inter-electrode-dimension. The difficulty of poling is mainly due to the high electric impedance and piezoelectric activities of the composites are lower than those of pure ceramics. Thus, the poling field and the poling temperature should be increased to facilitate poling of the ceramic particles in the composites. However, if the poling voltage is too high, the samples can be broken down or if a poling temperature is too high, the mechanical properties of the cement can be weakened. Therefore, improving the electrical conductivity of the cement matrix is one of the efficient methods to increase the polarization of the composite.

Carbon materials have excellent electrical properties and are often used to enhance the conductivity of other composites. Shifeng et al. investigated the effect of carbon black on the properties of 0-3 piezoelectric ceramic/cement composites (Shifeng et al., 2009). The composites were manufactured using sulphoaluminate cement and piezoelectric ceramic  $[0.08\text{Pb}(\text{Li}_{1/4}\text{Nb}_{3/4})\text{O}_3 \cdot 0.47\text{PbTiO}_3 \cdot 0.45\text{PbZrO}_3][\text{P}(\text{LN})\text{ZT}]$  as raw materials with a compression technique. The piezoelectric strain constant  $d_{33}$  of the composites with carbon black content was as shown in Fig.9. The piezoelectric strain constant at its maximum was 42% larger than that of the composite without carbon black when 0.3 wt% content of the carbon black was used, and decreased when the content of carbon black was beyond 0.3 wt%. The Maxwell-Wagner model can explain this trend. The following equation (1) gives the ratio of the electric field acting on the ceramic particles and matrix phases in a 0-3 piezoelectric composite with the conductivity (Blythe, 1979).

$$E_1/E_2 = \sigma_2/\sigma_1 \quad (1)$$

where  $\sigma_1$  and  $\sigma_2$  are the electric conductivity of the ceramic and the matrix, respectively. It is noteworthy that the electric field working on the ceramic particles is controlled by the ratio ( $\sigma_2/\sigma_1$ ). Because the conductivity of ceramic particles is much higher than that of the cement matrix,  $\sigma_2/\sigma_1$  is small. Thus, the addition of a small amount of a conductive material, such as carbon materials, decreases the impedance of the composite and increases the electric conductivity of the composite. As a result, the electric conductivity of the cement matrix increases, resulting in easier poling. Therefore, up to a suitable amount of carbon black addition, the piezoelectric constant  $d_{33}$  increases gradually, whereas with more than 0.3 wt% of the amount of carbon black added, the piezoelectric properties is decreased, because the higher voltage could not be established during the poling process. Gong et al. also reported the piezoelectric and dielectric behavior of 0-3 cement-based composites mixed with carbon black (Gong et al., 2009). They fabricated 0-3 cement-based composites from white cement, PZT powder and a small amount of carbon black and found similar results to those of a poling process of the composite at room temperature that was facilitated by the addition of

carbon black; the piezoelectric properties of the composite were improved. It was also found that when too much carbon black was added, the piezoelectric properties of the composite decreased, due to the conductive properties of the carbon black. Sun et al. also found that carbon fiber could be used for piezoelectric concrete (Sun et al., 2000).

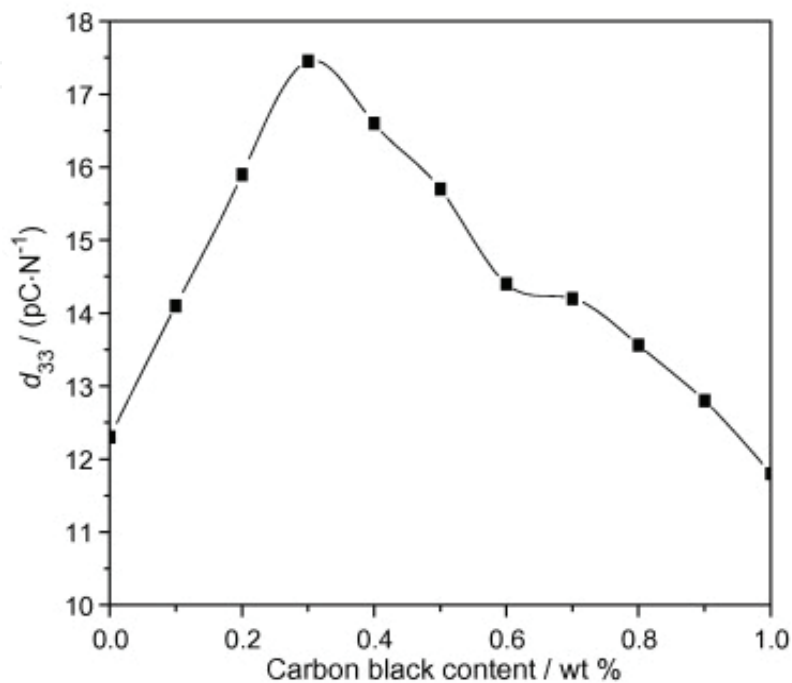


Fig. 6. Variation of piezoelectric strain constant  $d_{33}$  of the composites with carbon black content (Shifeng et al., 2009)

As for the piezoelectric cement composites, the piezoelectric properties of the polymer composites can be facilitated by addition of the conductive carbon materials. Sakamoto et al. reported acoustic emission (AE) detection of PZT/castor oil-based polyurethane (PU) with and without graphite doping (Sakamoto et al., 2002). The piezoelectric and pyroelectric properties of the composite increased with graphite doping, due to the enhanced conductivity/reduced resistance caused by graphite doping. Moreover, the piezoelectric coefficient  $d_{33}$  varied with the carbon content with similar behavior to that of the piezoelectric cement composites, as shown in Fig.7. As a result, two simulated sources of AE, ball bearing drop and pencil lead break, were detected better with the graphite doped PZT/PU composite. This can be also explained by the aforementioned Maxwell-Wagner interfacial mechanism.

Piezoelectric polymer composites can be also useful as mechanical damping composites (Hori et al., 2001). PZT/carbon black/epoxy resin composites were manufactured and their mechanical and damping properties were investigated. A measure of mechanical of damping intensity, the mechanical loss factor ( $\eta$ ), reached its maximum at a certain level of carbon black added and decreased above that as shown in Fig.8. In this composite, carbon black had an additional function: when the mechanical energy from vibrations and noises was transformed into electrical energy (current) by PZT, the electric current was conducted to an external circuit through CB powders and then dissipated as thermal energy through a resistor.

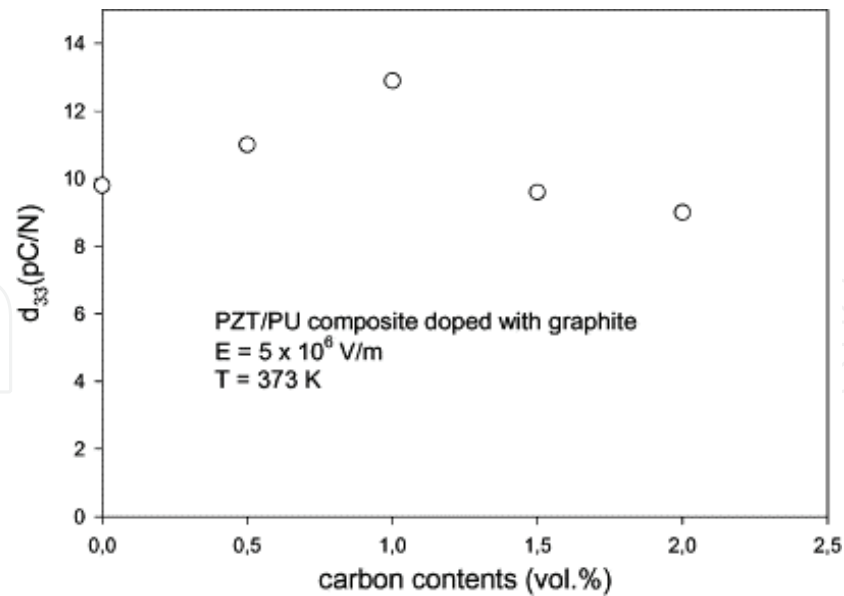


Fig. 7. Variation of the piezoelectric coefficient  $d_{33}$  with the carbon contents in the composite film (Sakamoto et al., 2002)

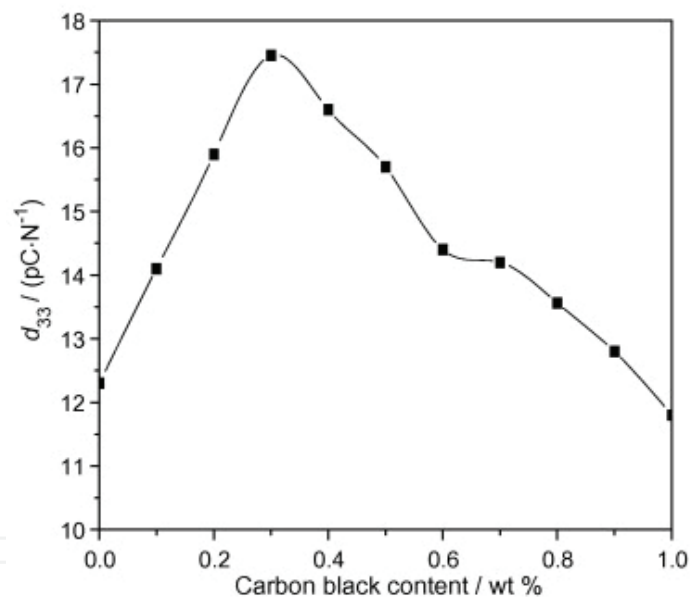


Fig. 8. Variation of piezoelectric strain constant  $d_{33}$  of the composites with carbon black content (Hori et al., 2001)

Unlike the studies described so far, Li et al. reported that piezoelectric material improve the properties of carbon materials (Li et al., 2010). The single crystal PMN-PT (lead magnesium niobate-lead titanate, which has a chemical formular of  $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$  and  $x[\text{PbTiO}_3]$ , was embedded in the two different activated carbons (NAC and HAC), and hydrogen adsorption of the composite was investigated. Hydrogen adsorption of the composite was enhanced due to an electric field generated from the piezoelectric material, and the amount of the enhancement was proportional to the charges generated by the piezoelectric materials. Therefore, higher hydrogen adsorption was achieved because higher pressure created more charges (Fig.9 and 10). Hydrogen adsorption at lower temperatures



was much greater than that at higher temperatures, because the electric field has a great effect on the bonding of hydrogen molecules more when the kinetic energy of the molecules is lower at lower temperatures (Fig.10).

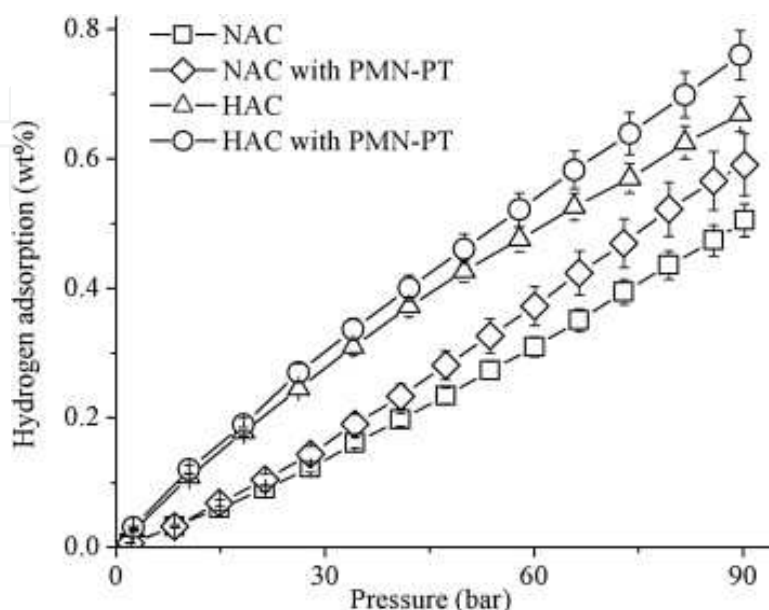


Fig. 9. PMN-PT effect on H<sub>2</sub> adsorption of NAC and HAC at 293 K under various pressures (Li et al., 2010)

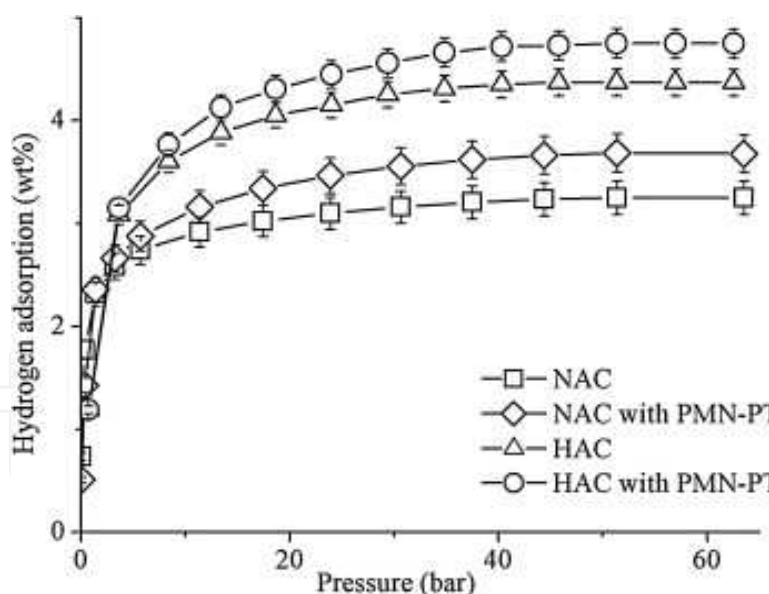


Fig. 10. PMN-PT effect on H<sub>2</sub> adsorption of NAC and HAC at 77 K under various pressures (Li et al., 2010)

## 5. Conclusion

In this chapter, carbon materials were introduced to assist the application of ferroelectric related materials. Ferroelectric-gate CNT transistors use the unique interfacial and electrical properties of CNTs to a longer data retention time of the transistor. In all of the piezoelectric

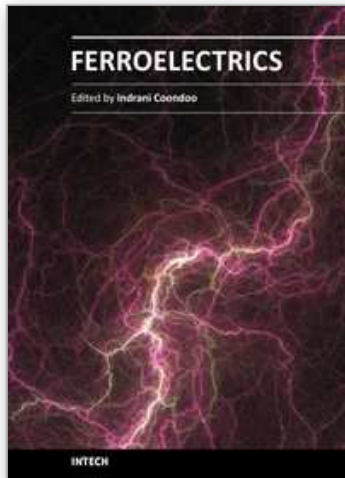
composites for different applications, up to a certain level of carbon materials added, the piezoelectric properties of the composites increased, as the content of carbon materials increased. But the piezoelectric properties decreased, as the content of carbon materials increased above that level. These behaviors can be explained by Maxwell-Wagner mechanism. Therefore, even if the carbon materials themselves do not have any ferroelectricity, the excellent electrical properties of carbon materials enable them to assist the applications of ferroelectric and related materials.

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## **Ferroelectrics**

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Ferroelectric materials exhibit a wide spectrum of functional properties, including switchable polarization, piezoelectricity, high non-linear optical activity, pyroelectricity, and non-linear dielectric behaviour. These properties are crucial for application in electronic devices such as sensors, microactuators, infrared detectors, microwave phase filters and, non-volatile memories. This unique combination of properties of ferroelectric materials has attracted researchers and engineers for a long time. This book reviews a wide range of diverse topics related to the phenomenon of ferroelectricity (in the bulk as well as thin film form) and provides a forum for scientists, engineers, and students working in this field. The present book containing 24 chapters is a result of contributions of experts from international scientific community working in different aspects of ferroelectricity related to experimental and theoretical work aimed at the understanding of ferroelectricity and their utilization in devices. It provides an up-to-date insightful coverage to the recent advances in the synthesis, characterization, functional properties and potential device applications in specialized areas.

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