

# DIELECTRIC PROPERTIES OF NICKEL CONTAINING HYDROGENATED AMORPHOUS CARBON FILMS PREPARED BY MICROWAVE PLASMA-ASSISTED DEPOSITION TECHNIQUE

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Received: January 22, 2007

**Abstract.** Nickel/hydrogenated amorphous carbon (a-C:H) composite films have been deposited at room temperature on nickel coated (100)-oriented single crystal silicon substrates by combining sputter-deposition of metal and microwave plasma-assisted chemical vapor deposition of carbon from argon-methane mixtures of various concentrations. The sputtering power was varied from 0 W to 45 W. The films have been deposited on either grounded substrates or substrates biased to  $-10$  V. The dielectric properties of films were investigated as functions of the frequency and temperature varying from 0.1 Hz to 1 MHz and from  $-150$  °C to 175 °C, respectively. Pure a-C:H films exhibited a dielectric constant of 2.6 at a wide range of frequency. For Ni/a-C:H composite films of 360 nm in thickness containing 19% of nickel the dielectric constant at a frequency of 1 Hz was higher than 300. The value of the dielectric constant of these composite films was observed to decrease from above 300 to 200 as the frequency increased from 1 Hz to 10 kHz. The effect of temperature and frequency as well as nickel content in the films on the dielectric properties is discussed.

## 1. INTRODUCTION

Over the last few years materials of high permittivity were thoroughly investigated owing to their usefulness in the microelectronics as capacitors or memory devices. Most of the reports were related to perovskites and/or ferroelectric materials, as example [1-3], and some about their composites [4]. At most cases, the major disadvantage in the production of films exhibiting high dielectric constant (high  $k$  materials) is the substrate temperature which needs to be in the range of 400-600 °C. Simultaneously there were many works related to the dielectric properties of carbon-based films but

most of them concerned low permittivity [5,6]. Relatively little results were published on the research of carbon based composite films showing elevated dielectric constant values [7,8]. The metallic particles introduced into amorphous carbon (or carbon based) matrix allow obtaining relatively high dielectric constant [7,8]. In a previous study [9] the mechanical properties and friction behavior of nickel/hydrogenated amorphous carbon composite films were investigated as functions of carbon content. In this work it will be shown that also carbide phase ( $\text{Ni}_3\text{C}$ ) may improve the dielectric constant of films.

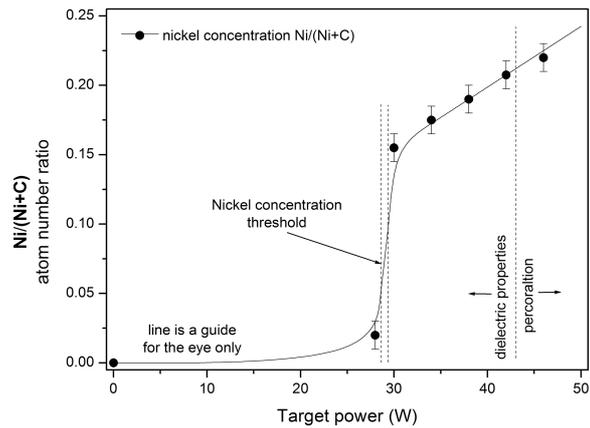
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## 2. EXPERIMENTAL

Thin films of nickel containing amorphous carbon (Ni/a-C:H) have been deposited at room temperature in a distributed electron cyclotron resonance (DECR) microwave plasma reactor [10] evacuated to the base pressure of  $\sim 2 \cdot 10^{-4}$  Pa. By introducing metal target into the chamber such a system combines advantages of microwave plasma enhanced chemical vapor deposition (MW PECVD) and sputtering. The circular nickel target (120 mm in diameter) was DC negatively polarized and sputtered in MW generated plasma gas mixtures consisting of 30 vol.% of argon and 70 vol.% of methane. The dissipated microwave power was 400 W. The sputtering power was tuned to 30–45 W to obtain samples with different nickel contents. The total pressure was kept constant at 0.13 Pa. The (100) oriented single crystal silicon wafers (rectangular in shape 10 mm by 35 mm) covered with a nickel layer of 300 nm in thickness were used as substrates. The resistivity of nickel (bottom) electrode was  $14 \mu\Omega\text{cm}$ . Nickel are used as bottom electrode owing the ease of substrate production (the same chamber was used) and these films were found to be tightly adherent to Ni/a-C:H films for preliminary experiments. The substrates have been placed on the water cooled holder, situated at a distance of 110 mm from the target and kept at the floating potential equal to  $-10$  V. The film thickness was in the range 300 nm to 380 nm and was found from the edge profile of masked area measured by stylus profilometer.

The Ni/a-C:H films deposited on uncoated silicon substrates were analyzed by wave dispersive X-ray spectrometer (WDXS) assuming that the chemical composition of the films is not affected by the type of the substrate (nickel or silicon). The nickel content in Ni/a-C:H films expressed by the Ni/(Ni+C) atom number ratio was equal to  $\sim 15.5$ ,  $\sim 17.3$ , 19, and 21%. The hydrogen to carbon atom number ratio (H/C) was equal to about 0.38–0.40 and was not depending on the composition of the film in this range of nickel content [9]. The hydrogen content was measured by elastic recoil detection analysis (ERDA). The upper gold electrodes were deposited by evaporation. The size of upper electrode was 1.55 mm in diameter and 330 nm in thickness. The diameter of the upper electrodes can be considered as infinitely higher than the film thickness in respect to the electric measurement accuracy, so the edge effects (like stray and parasitic capacities) may be ignored. For the elec-



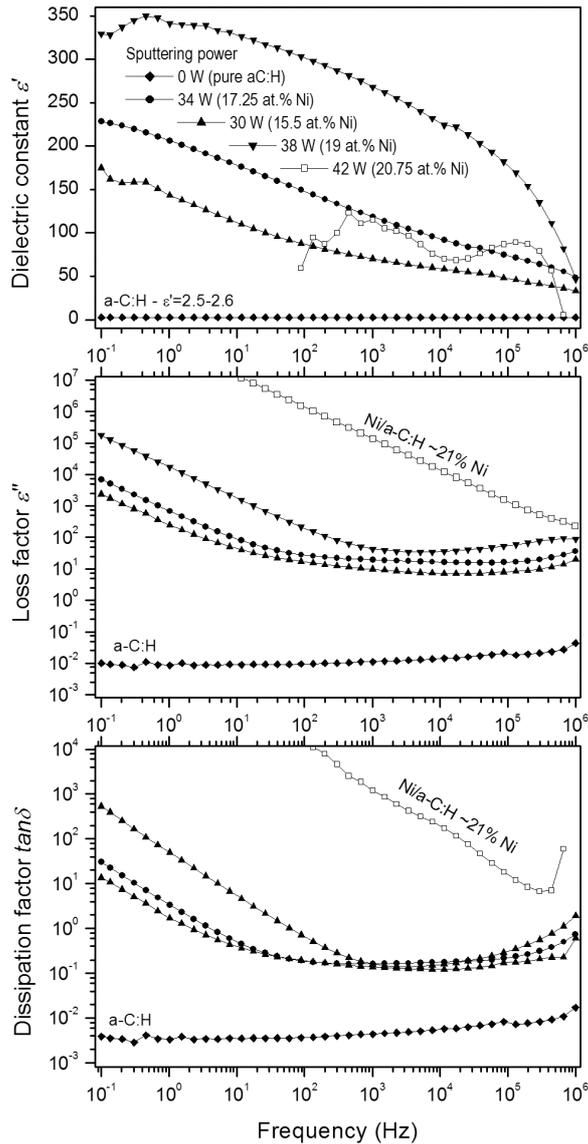
**Fig. 1.** Chemical composition of films as a function of sputtering power.

tric properties measurements the samples were placed in a metallic container enabling temperature control in the range from  $-180$  °C to  $+200$  °C in dry nitrogen ambient. A Novocontrol Alpha BDS 20 dielectric spectrum analyzer was used for electric measurements within a range of frequency from 0.1 Hz to 1 MHz (isothermal) and within a range of temperature from  $-150$  °C to  $+175$  °C at test voltage (RMS) equal to 0.1 V.

## 3. RESULTS AND DISCUSSION

### 3.1. Chemical composition and structure of films

From the previous research [9] it was found, that in this range of nickel concentrations (15.5% to 21%) whole nickel atoms are bonded to carbon atoms, creating nickel carbide  $\text{Ni}_3\text{C}$  crystallites of size lower than 2 nm. The chemical composition of films as a function of the sputtering power is presented in Fig. 1. There are four regions which can be distinguished: a) low nickel content films, containing little amount of nickel carbide  $\text{Ni}_3\text{C}$  (approx up to 2–3%), b) threshold of the nickel concentration where nickel content increases quickly up to approximately 15%, c) region of linear increase in nickel content, and d) region of conductive films for nickel concentrations above  $\sim 21\%$ . It is suspected that nickel concentration threshold appears due to the contamination of the target (poisoning) with carbon. The sputtering power lower

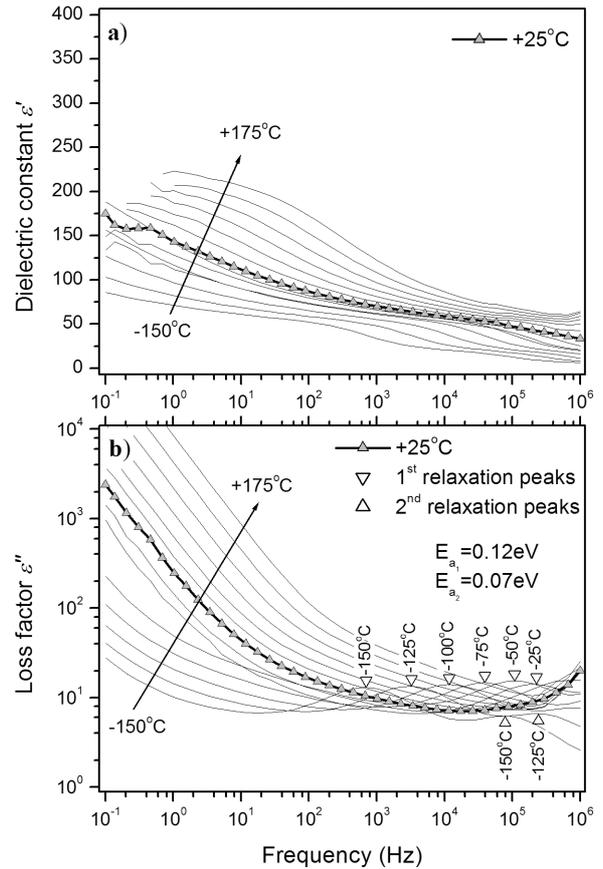


**Fig. 2.** Dielectric constant ( $\epsilon'$ ), the loss factor ( $\epsilon''$ ) and the dissipation factor ( $\tan\delta$ ) for films as functions of the frequency at 25 °C.

than 30 W is not high enough for resputtering of carbon deposited on the target surface, thus little amount of nickel is sputtered from the target. That is also the reason of using Ar/CH<sub>4</sub> mixtures for deposition instead of pure CH<sub>4</sub>.

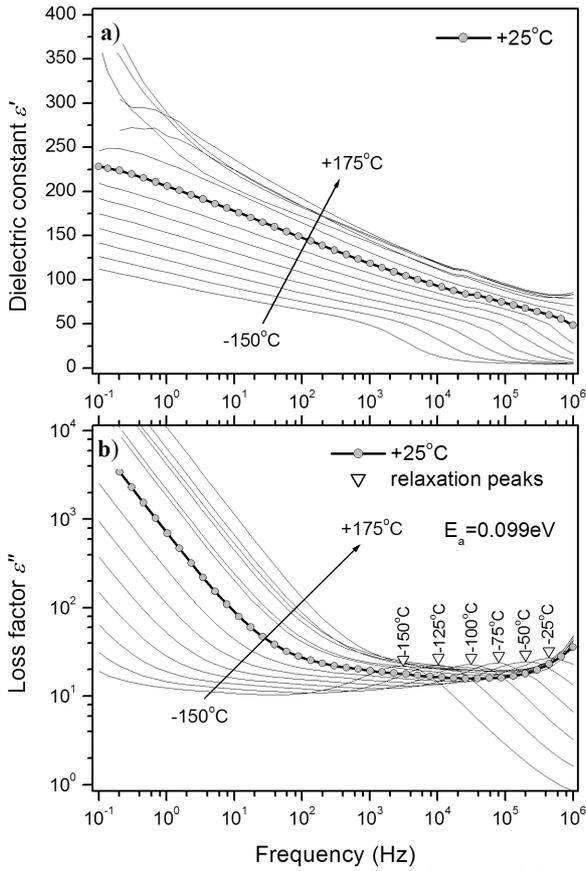
### 3.2. Dielectric properties of films

The dielectric constant ( $\epsilon'$ ), the loss factor ( $\epsilon''$ ) and the dissipation factor ( $\tan\delta$ ) for Ni/a-C:H films at room temperature are shown in the Fig. 2 as functions of the frequency. There are four curves rep-

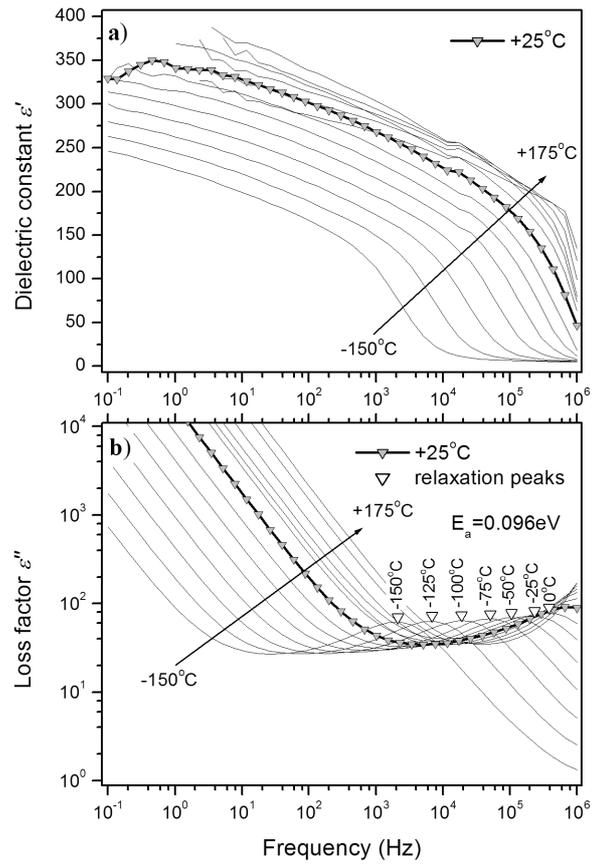


**Fig. 3.** Dielectric constant and loss factor of films containing 15.5 at.% of nickel as functions of the frequency at different temperatures.

resenting films of various nickel contents and one for nickel free films (reference sample). In the context of researches on low dielectric constant (low  $k$ ) materials [5,6,11,12] these pure a-C:H films seem to be of interest. Those films showed a dielectric constant at level 2.6 being almost independent ( $\pm 0.1$ ) of the frequency changing from 0.1 Hz to 1 MHz. The incorporation of conductive particles into a dielectric matrix leads to the increase in dielectric constant [7,13,14]. This phenomenon is induced by high polarizability of conductive materials. As it is shown in Fig. 2 the dielectric constant increases with increasing nickel content and reaches a maximum value (over 300 at frequencies lower than 100 Hz) for films containing 19% of nickel. These films possess also the most flat characteristic of dielectric constant. The decrease in dielectric constant with increasing frequency is also lower than for films with lower nickel content. A further increase in nickel content (~21%) leads to



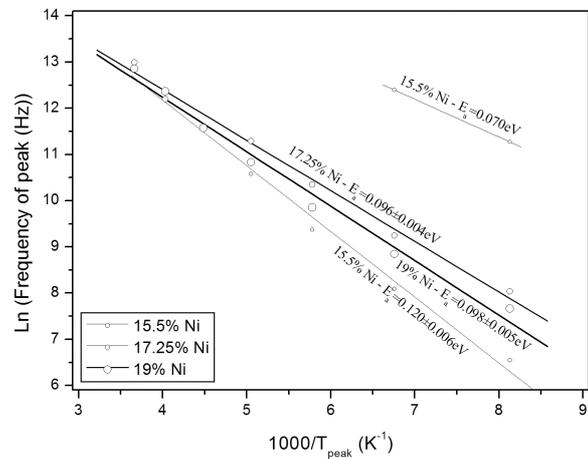
**Fig. 4.** Dielectric constant and loss factor of films containing 17.25 at.% of nickel as functions of the frequency at different temperatures.



**Fig. 5.** Dielectric constant and loss factor of films containing 19 at.% of nickel as functions of the frequency at different temperatures.

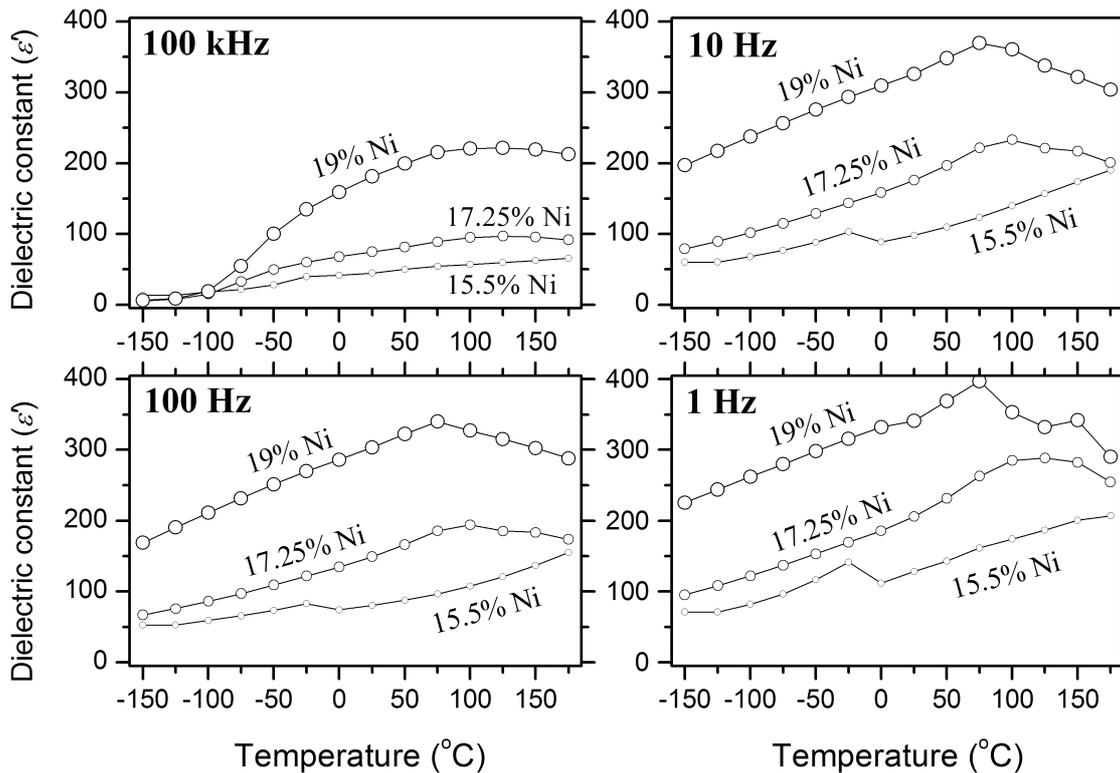
dielectric instabilities and finally to dielectric breakdown at frequencies below 100 Hz. Thus, it may be assumed that the percolation appears at nickel concentration close to 21%, since films containing ~22% of nickel show fully conductive properties.

The values of permittivity for Ni/a-C:H films with nickel content up to 19% films were higher than that of reported by Huang *et al.* [7], however the amount of molybdenum content in those Mo/C:H films was in the range 0.1 to 3 at.%. On the other hand, values of permittivity of those Mo/a-C:H films were strongly dependent on the frequency. The decrease in the dielectric constant for Mo/C:H as the frequency varied from 100 Hz to 1 kHz was more than ten times. For Ni/a-C:H films the decrease of dielectric constant in the range of frequency from 0.1 Hz to 100 kHz was less than two times (Fig. 2a). The loss factor for Ni/a-C:H films was strongly increased (several orders) by the presence of Ni<sub>3</sub>C phase when compared to reference samples of pure a-C:H films (Fig. 2b), particularly



**Fig. 6.** Arrhenius plot of relaxation mechanism for Ni/a-C:H films containing 15.5%, 17.25%, and 19% of nickel.

at lower frequencies (0.1 Hz to 100 Hz). The increase at low frequencies is considered to be caused by DC conductivity. As a consequence the dissipation factor for Ni/a-C:H films was degraded



**Fig. 7.** Dielectric constant as functions of temperature at a given frequency and for given nickel content in the films.

(Fig. 2c). Thanks to low variation of dielectric constant as the frequency increased the dissipation factor values were moderate at the frequencies higher than 1 kHz. The loss factor as well as the dissipation factor for Ni/a-C:H films with nickel content higher than 19% reached very high values due to close-to-percolation structure (Figs. 2b-2c).

The dielectric constant ( $\epsilon'$ ) and the loss factor ( $\epsilon''$ ) as functions of the frequency at different temperatures are shown in Figs. 3-5 for films containing 15.5%, 17.25%, and 19% of nickel, respectively. For pure a-C:H films (reference sample) the influence of temperatures on the dielectric constant and the loss factor is very low ( $\epsilon'$  – few percent;  $\epsilon''$  – within one order). For nickel containing a-C:H films the influence of temperature on these properties was significant. As the temperature increases both, the dielectric constant and the loss factor increase as well. For Ni/a-C:H films containing 15.5% to 19% of nickel at negative temperatures (varied from  $-150^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ ) and in the range of frequencies varied from 1 kHz to 1 MHz a relaxation mechanism was clearly observed (Fig. 3b-5b). With in-

creasing temperature in this range, the relaxation peaks (loss factor curves) shifted to higher frequencies. This relaxation mechanism induced the decrease in dielectric constant at a given temperature with increasing frequency. The frequency of relaxation peak in the loss factor curve for a given temperature was slightly dependent on the nickel content (Fig. 3b-5b). For films containing 15.5% of nickel another relaxation mechanism was observed. It appeared as a peak in loss factor curve (Fig. 3b) at high frequencies (above 100 kHz) and at lowest temperatures ( $-150^{\circ}\text{C}$  and  $-125^{\circ}\text{C}$ ) (Fig. 3). Considering the dielectric constant curves of lowest temperatures ( $-150^{\circ}\text{C}$  and  $-125^{\circ}\text{C}$ ) for Ni/a-C:H films the sudden decrease in  $\epsilon'$  values appeared as the frequency varied from 1 kHz to 10 kHz. The dielectric constant at those temperatures and higher frequencies was almost constant and of value close to that of pure a-C:H. The exception was for films containing 15.5% of nickel. We believe this exception was caused by the presence of the second relaxation mechanism (Fig. 3b). Relaxation mechanism showed in Figs. 3b-5b

obeyed to an Arrhenius behavior (Fig. 6). The activation energy of the relaxation observed for Ni/a-C:H films containing 19% and 17.25% of nickel were at the same level of 0.1 eV. For films containing 15.5% of nickel this activation energy was slightly higher (0.12 eV) but can be considered as caused by the same mechanism as for films with higher nickel content. As the Ni/a-C:H films are consisted of conductive nickel carbide ( $\text{Ni}_3\text{C}$ ) particles embedded into dielectric matrix of hydrogenated amorphous carbon the interfacial polarization is the most probably phenomenon for relaxation, which is commonly observed in two phase materials [7, 13]. The other relaxation mechanism was observed for films containing 15.5% of nickel. The activation energy was estimated on the basis of only two points, thus the mechanism of this relaxation cannot be clearly identified.

As shown in Figs. 3a-5a the dielectric constant depends on both, the temperature and nickel content for a given frequency. In a purpose of better legibility the dielectric constant functions for films of different nickel content at given frequencies as functions of temperature are plotted in Fig. 7. The shapes of curves of dielectric constant as functions of temperature for films containing 19% and 17.25% of nickel are similar. As the temperatures varied from  $-150\text{ }^\circ\text{C}$  to  $+75\text{ }^\circ\text{C}$  the increase in dielectric constant was observed. Further increase of temperature led to the decrease in the dielectric constant. The increase of dielectric constant with increasing temperature was probably caused by thermal activation of electrons from conductive particles. Simultaneously the space charge is accumulated at the interface between the film and the electrode. When the temperature equal to  $+100\text{ }^\circ\text{C}$  was reached this accumulated space charge became more significant compared to the polarizability of the film, thus the dielectric constant decreases.

For films containing 15.5% of nickel as temperature varied from  $-50\text{ }^\circ\text{C}$  to  $-25\text{ }^\circ\text{C}$  the decrease in dielectric constant was observed (Fig. 7 – 100 Hz, 10 Hz, 1 Hz). As the temperature was increasing in other ranges the dielectric constant was increasing. This decrease in the dielectric constant was also observed for pure a-C:H films at whole range of frequency and as temperature varied from  $-25\text{ }^\circ\text{C}$  to  $25\text{ }^\circ\text{C}$ .

#### 4. CONCLUSIONS

Nanostructured nickel containing hydrogenated amorphous carbon films were produced by a mi-

crowave plasma enhanced chemical vapor deposition of carbon from  $\text{Ar}/\text{CH}_4$  mixture combined with sputtering of a nickel target. The dielectric properties of those Ni/a-C:H composite films were studied in a wide range of temperature ( $-150\text{ }^\circ\text{C}$  to  $+175\text{ }^\circ\text{C}$ ) and frequency (0.1 Hz to  $10^6$  Hz). The increase in dielectric constant for Ni/a-C:H films was of two orders compared to reference samples of pure a-C:H (deposited from pure methane) and reached values over 300. The significant change in the dielectric constant for these films was observed as the temperature varied showing that the conduction processes were thermally activated. Relaxation process for Ni/a-C:H films was identified to be of interfacial effects of  $\text{Ni}_3\text{C}$  nanoparticles dispersed in a-C:H matrix.

#### ACKNOWLEDGEMENTS

The financial support from French Government in the frame of the Polonium program and cotutelle fellowship is gratefully acknowledged.

#### REFERENCES

- [1] S.Zhitang and L.Chenglu // *Appl. Surf. Sci.* **158** (2000) 21.
- [2] H.Xu, H.Zhu, K.Hashimoto, T.Kiyomoto, T.Mukaigawa, R.Kubo, Y.Yoshino, M.Noda, Y.Suzuki and M.Okuyama // *Vacuum* **59** (2000) 628.
- [3] Q.Tang, M.Shen and L.Fang // *Solid State Communications* **135** (2005) 707.
- [4] L.Tang, P.Du, G.Han, W.Weng, G.Zhao and G.Shen // *Surf. Coat. Technol.* **167** (2003) 177.
- [5] S.P.Louh and M.H.Hon // *Diamond Rel. Mater.* **14** (2005) 1915.
- [6] Xungao Zhang, Ying Liu and Jingui Qin // *Carbon* **42** (2004) 885.
- [7] Q.F.Huang, S.F.Yoon, E. Rusli, Q.Zhang and J.Ahn // *Thin Solid Films* **409** (2002) 211.
- [8] J.E.Atwater and R.R.Wheeler Jr. // *Carbon* **41** (2003) 1801.
- [9] S.Kukielka, W.Gulbiński, Y.Pauleau, S.N.Dub and J.J. Grob // *Surf. Coat. Technol.* **200** (2006) 6258.
- [10] M.Pichot and J.Pelletier, In: *Microwave Excited Plasma, Plasma Technology, vol. 4, Ch.14*, ed. by M. Moisan and J. Pelletier (Elsevier, Amsterdam, The Netherlands, 1992), p. 419.
- [11] E.Rusli, M.R.Wang, T.K.S.Wong, M.B.Yu and C.Y.Li // *Diamond Rel. Mater.* **15** (2006) 133.

- [12] C.Zuniga, A.Torres and A.Kosarev // *J. Non-Crystalline Solids* **329** (2003) 174.
- [13] P.Canet, C.Laurent, J.Akinnifesi and B.Despax // *J. Appl. Phys.* **72** (1992) 2423.

- [14] P.Gonon and A.Boudefel // *J. Appl. Phys.* **99** (2006) 024308.