# Effects of the methane content on the characteristics of diamond like carbon films produced by sputtering

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In this work, hydrogenated carbon films were sputter deposited at low temperatures using different Ar-CH$_4$ mixtures. The deposition rate of the films increases with up to a factor of 6 when comparing a CH$_4$ rich mixture to a pure Ar plasma. At the same time, the sp$^3$ carbon content is much higher when CH$_4$ is added to the Ar, and as a consequence the resistivity increases, with approximately 6 orders of magnitude, and the breakdown electric field increases with approximately a factor of 3. Another attractive feature of the films deposited with a CH$_4$ rich plasma, is the low dielectric constant, down to 1.8 for a pure CH$_4$ plasma. The RMS roughness of a 1 micrometer thick film is as low as 1.6 nm. All these features make this technique interesting for depositing intermetallic layers.

## 1. Introduction

Hydrogenated carbon films have several applications in different industrial areas, because of their high density, hardness, chemical inertness, smoothness, etc [1, 2]. In the microelectronic industry, these diamond like carbon (DLC) films have a great potential as gate dielectric, intermetal dielectric and passivation layers.

These films can be deposited by several techniques, such as Chemical Vapour Deposition (CVD), mass selected ion beam systems, laser ablation and sputtering [3]. The film characteristics depend on several different deposition process parameters, such as the gas composition and pressure, the substrate temperature, the energy of the impinging ions etc [2]. The presence of hydrogen in the gas phase promotes the formation of sp$^3$ C structures [4]; sp$^3$ rich hydrogenated carbon films have higher electrical resistivities and higher breakdown voltages [5]. An extra advantage of DLC films is their relatively low dielectric constant [1], what makes them extremely interesting for intermetal dielectric layers in multilayer metal integrated circuits [6]. For microelectronic purposes, these films are usually obtained by PECVD techniques using different hydrogen sources, such as H$_2$ and CH$_4$ [1,3,7], and by reactive sputtering of carbon, adding one of these gases to Ar [1,8].

Important characterization techniques for these films are: for physical-chemical characterization the traditional techniques are Fourier Transform Infrared Spectroscopy (FTIR) [5,9,10] and Raman Spectroscopy [8,10,11]; for electrical characterization, the use of I-V and C-V curves are the most common [12].

In this work, the influence of the CH$_4$ content in an Ar based carbon sputtering system on the deposition rate, dielectric constant, chemical composition, electrical resistivity and breakdown field of the hydrogenated carbon films, is studied.

## 2. Experimental

The films were produced in a reactive RF magnetron sputtering system. The target is a 99.9999% pure, 6 inch diameter, graphite plate, located at 100 mm from the substrate. A pump system composed of a rotary vane and a turbo-molecular pump, was used to attain a residual pressure of $4.10^{-6}$ Torr. The process pressure was kept constant at $5.10^{-3}$ Torr. The Ar + CH$_4$ total flow was also kept constant at 70 sccm; the CH$_4$ content was varied from 0% to 100% of the total flow. The RF power was applied at 13.56 MHz and kept constant at 150 W. The substrate temperature was not controlled, but measured with a type K thermocouple, its temperature never exceeded 90°C.

Two types of wafers were used : traditional three inch diameter, 280 μm thick, p-type, (100), test quality silicon wafers with resistivities in the range of 10-20 Ωcm, and three inch diameter, 400 μm thick, double side polished, p-type, prime quality wafers with a resistivity of 5 Ωcm. The high quality wafers are used for FTIR measurements, the lower quality wafers for the other tests. All were submitted to a Piranha clean, followed by a diluted HF dip, before film deposition.

The film thickness was measured with a Dektak 3030 step height meter and a Rudolph AUTOEl-NIR3 ellipsometer.

The chemical composition was measured with a Bio-RAD FTS 40 Fourier Transform Infra Red (FTIR) spectrometer
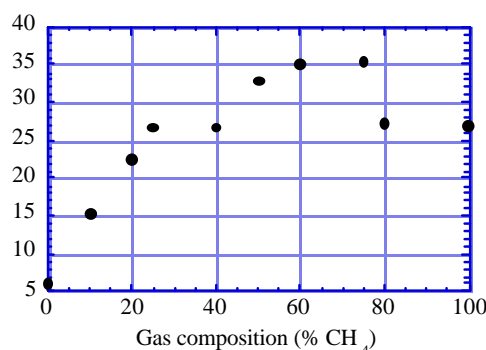
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Fig. 1: DLC film deposition rate as a function of $CH_4$ percentage of total gas flow.



Fig. 2: FTIR spectra (detail) for the films obtained at: (a) 100% $CH_4$, (b) 75 % $CH_4$, (c) 50 % $CH_4$, (d) 25 % $CH_4$, and the Bessel deconvolution fit for the 100% $CH_4$ sample (dashed lines).

The surface roughness of the deposited films was determined using a Atomic Force Microscope (AFM) Nanoscope III from Digital. The analyzed areas were 5 μm by 5 μm and 25 μm by 25 μm.

For C-V and I-V measurements, electrical contacts were deposited at the front side of the wafer, by aluminum evaporation through a mechanical mask in order to obtain 300 nm thick, 1mm diameter cylinders. At the back side of the wafer, a 500 nm thick aluminum film was evaporated.

The dielectric constant was determined with a HP 4280 high frequency C-V meter and the electrical conductivity with a HP 4140A pico-amperemeter.



Fig. 3: Ratios of the sum of the areas of the $sp^3$ $CH_x$ peaks/area of the $sp^2$ CH peak, as a function of $CH_4$ percentage of total gas flow

### 3. Results and Discussion

Figure 1 shows the deposition rate of the amorphous hydrogenated carbon as a function of $CH_4$ flow.

The deposition rate increased substantially from 5nm/min to 25 nm/min, as the percentage of $CH_4$ increased from 0 to 30%. From this point, the deposition rate increased more slowly until it reached a maximum of 36 nm/min at 70% $CH_4$ content.

Then it decreased again to a value of 27 nm/min for a pure $CH_4$ sputtering gas. Using a $CH_4$ rich sputtering process, a 1 μm thick film can be deposited in less than 30 minutes, whereas it would take up to 167 minutes using the pure Ar process.

The process time was varied from 1 minute to 1 hour and the deposition rate of the investigated processes remained constant.
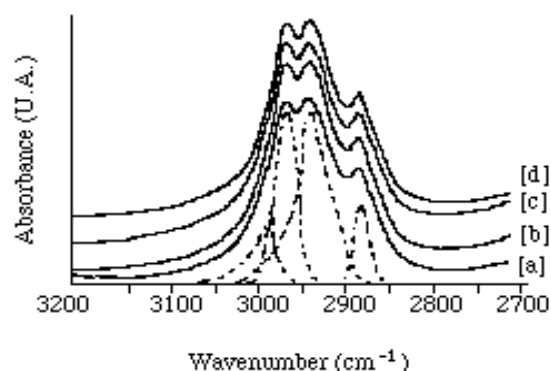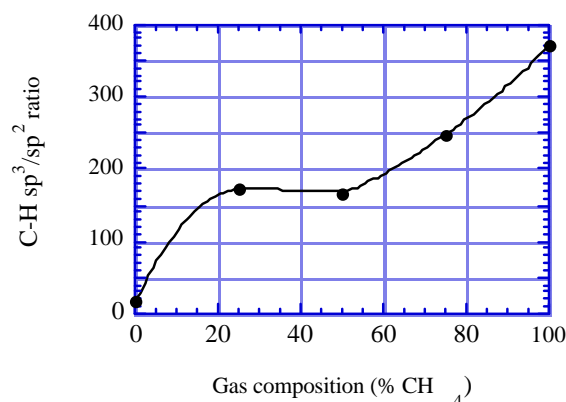
Figure 2 shows a detail of the performed FTIR analyses, showing the different $C-H_x$ $sp^2$ and $sp^3$ peaks for the different $CH_4$-Ar mixtures and the Bessel deconvolution fit for the 100% $CH_4$ sample. This convolution shows the following peaks : $sp^3$ $CH_3$ at 2875 $cm^{-1}$, $sp^3$ $CH_2$ at 2920 $cm^{-1}$, $sp^3$ $CH_3$ at 2960 $cm^{-1}$ and $sp^2$ CH at 3000 $cm^{-1}$ [5,7].

In order to quantify the results of the FTIR analyses, Bessel deconvolutions were performed on the FTIR spectra obtained from the different samples and the area of the $sp^2$ CH peak was compared with the sum of the areas of the three $sp^3$ peaks. The influence of the $CH_4$ content of the plasma on the ratios of the sum of the areas of the three $sp^3$ peaks to the area of the $sp^2$ CH peak, is shown in figure 3: when introducing $CH_4$ to the plasma, the ratio of the $sp^3$ peak areas to the $sp^2$ peak area, increases with the $CH_4$ concentration.

This indicates that the presence of $CH_4$ promotes very strongly the formation of $sp^3$ type carbon bond.

Figure 4 shows that the electric resistivity of the films behaves in a similar way as the $sp^3/sp^2$ ratio : when $CH_4$ is added, the resistivity increases with 6 orders of magnitude compatible with the much higher $sp^3$ type carbon than $sp^2$ type carbon concentration of these films.

Figure 5 shows that the breakdown electric field of the samples is determined by the $CH_4$ content in the mixture in approximately the same way as the electrical resistivity and the $sp^3/sp^2$ ratio. We suppose that the point at 70% had some anomaly ( e.g. a weak point ). In general, one may conclude that for mixtures with at least 30% $CH_4$, the breakdown field is at least three times higher than for the pure Ar plasmas.

The FTIR, resistivity and breakdown field caracterizations of the deposited films indicate that the films with a certain amount of $CH_4$ in the plasma, contain much more diamond like carbon (DLC) structures than the films which were deposited by pure sputtering of the carbon target, which are primarily of the graphite type carbon. Because of the higher DLC content in the deposited films, their resistivity and the breakdown electrical field are much higher.
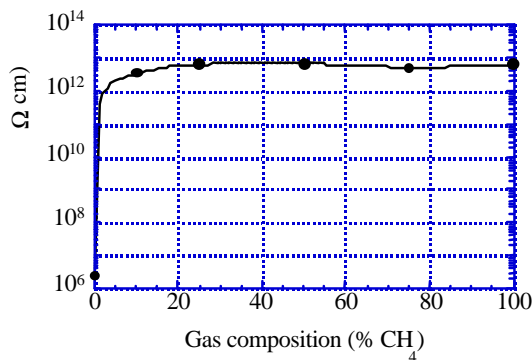


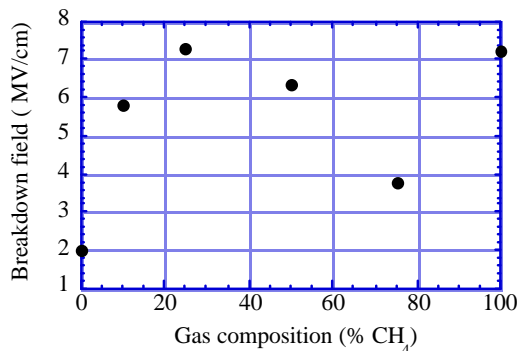Fig. 4: Resistivity as a function of $CH_4$ percentage of total gas flow.



Fig. 5: Breakdown electrical field as a function of $CH_4$ percentage of total gas flow
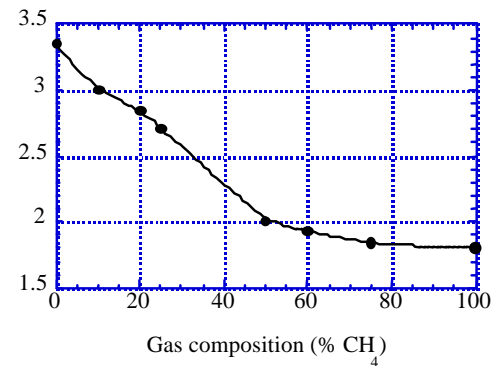


Figure 6: Dielectric constant (k) as a function of $CH_4$ percentage of total gas flow
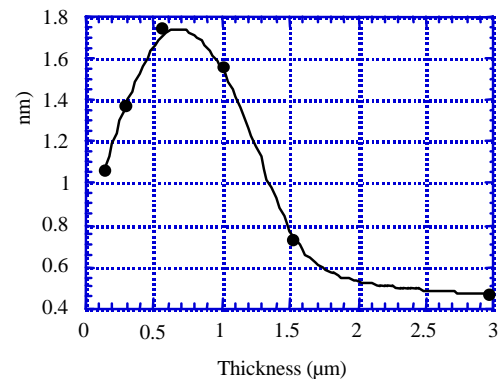


Figure 7: RMS roughness as a function of the thickness of the carbon films deposited with 100 % $CH_4$

Besides these traditional characteristics, the dielectric constant was also determined as a function of $CH_4$ content and the result is shown in figure 6. This figure shows that the dielectric constant decreases with nearly a factor of 2 from a pure Ar to pure $CH_4$ plasma.

The variation of the deposited film surface roughness in function of the thickness of the carbon films is shown in figure 7. These films were deposited on Si wafers with RMS roughness of 0.16 nm; the roughness level increases slightly up to 1.8 nm for a 0.6 μm thick film and decreases down to 0.7 nm for a 3 μm thick film. These results were independent of the size of the scanned area.

Using a process of 50% $CH_4$-50% Ar, one can deposit in 30 minutes, at a temperature lower than 90°C, a 1 micron thick layer, with resistivity of $8 \times 10^{12}$ Ohm cm, breakdown electric field of 6.4 MV/cm and dielectric constant of 2. These characteristics justify the use of these kinds of films as intermetallic dielectric layers [12]. Using a 100% $CH_4$ process, the deposition time has to be approximately 40 minutes, but the dielectric constant is somewhat lower at 1.8.

The RMS surface roughness of these films remains lower than 1.8 nm. In comparison, thermal silicon dioxide has a breakdown voltage of around 12 MV/cm, but can not be used after metal deposition on the wafer. PECVD deposited silicon dioxide, the traditional intermetal layer material, has a breakdown voltage which varies in the range of 3 MV/cm to 10 MV/cm, while its electric resistivity varies in the range of $10^{14}$ Ohm cm to $10^{16}$ Ohm cm. However, the dielectric constant of silicon dioxide is approximately 3.8. Therefore, the use of the $CH_4$ rich plasma sputtered dielectric films is extremely interesting as an intermetal layer where a low dielectric constant decreases the parasitic capacitances between the interconnect lines and therefore increases the speed of the integrated circuit.

## 4. Conclusions

Dielectric carbon films were sputter deposited at low temperatures using a graphite target with different Ar-$CH_4$ plasmas. Increasing the $CH_4$ content of these plasmas increases the deposition rate of the films with up to a factor of 6.

FTIR characterization showed that the films deposited with $CH_4$ containing plasmas are much richer in $sp^3$ type carbon than when deposited with pure Ar plasmas. This results in an increased electric resistivity, of the order of $10^{13}$ $\Omega$cm, and breakdown electric field, of approximately 7 MV/cm.

Besides, the dielectric constant decreases with increasing $CH_4$ concentration, down to 1.8 for a pure $CH_4$ plasma. The RMS surface roughness of the deposited films is always lower than 1.8 µm. All these characteristics indicate the possible use of these films for intermetal dielectric layers.

## Acknowledgements

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