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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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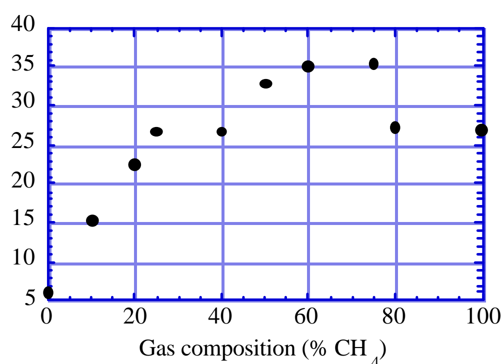

Fig. 1: DLC film deposition rate as a function of CH_4 percentage of total gas flow.

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.

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.

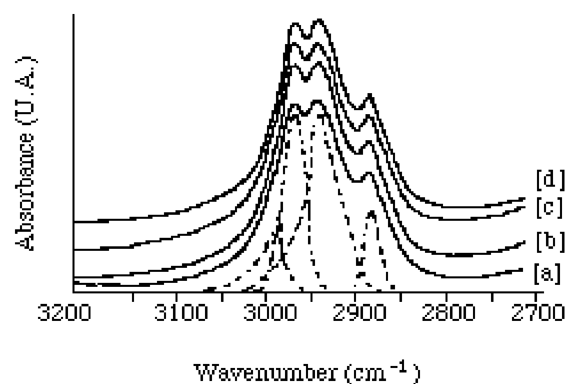

Fig. 2: FTIR spectra (detail) for the films obtained at: (a) 100% CH_4, (b) 75 % CH_4, (c) 50 % CH_4, (d) 25 % CH_4, and the Bessel deconvolution fit for the 100% CH_4 sample (dashed lines).

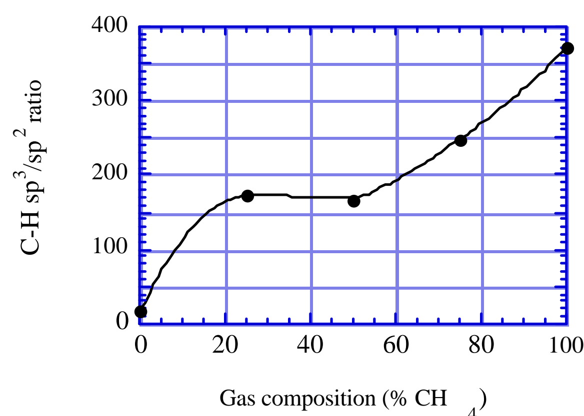

Fig. 3: Ratios of the sum of the areas of the sp^3 CH_x peaks/area of the sp^2 CH peak, as a function of CH_4 percentage of total gas flow

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.

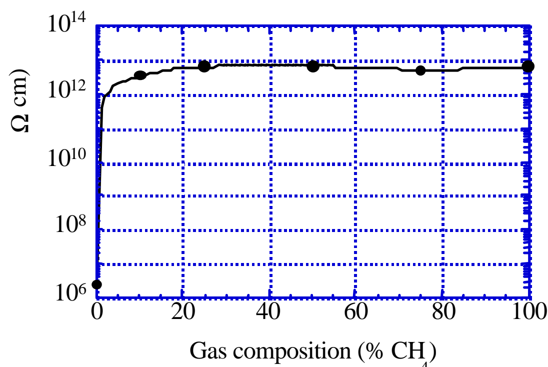

Fig. 4: Resistivity as a function of CH_4 percentage of total gas flow.

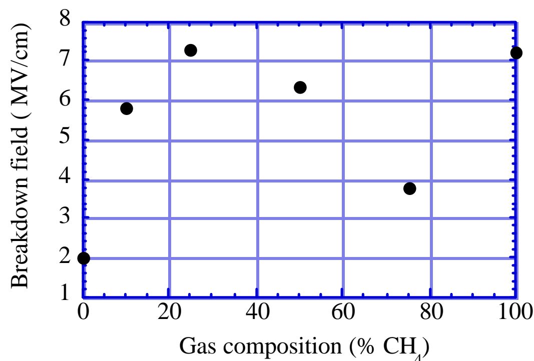

Fig. 5: Breakdown electrical field as a function of CH_4 percentage of total gas flow

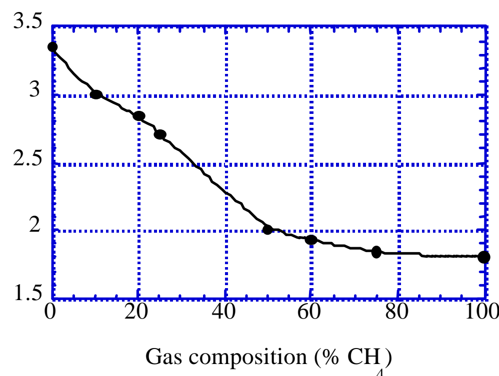

Figure 6: Dielectric constant (k) as a function of CH_4 percentage of total gas flow

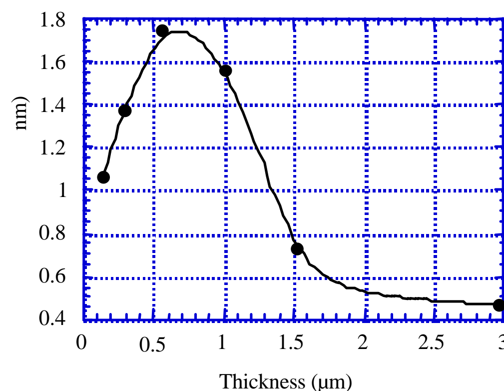

Figure 7: RMS roughness as a function of the thickness of the carbon films deposited with 100 % CH_4

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 $8x10^{12}$ 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} Ωcm, 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.

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