

# Characterization of amorphous hydrogenated carbon films deposited by MFPUMST at different ratios of mixed gases

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**Abstract.** Amorphous hydrogenated carbon films (*a*-C:H) on *p*-type (100) silicon wafers were prepared with a middle frequency pulsed unbalanced magnetron sputtering technique (MFPUMST) at different ratios of methane–argon gases. The band characteristics, mechanical properties as well as refractive index were measured by Raman spectra, X-ray photoelectron spectroscopy (XPS), nano-indentation tests and spectroscopic ellipsometry. It is found that the  $sp^3$  fraction increases with increasing Ar concentration in the range of 17–50%, and then decreases when Ar concentration exceeds 50%. The nano-indentation tests reveal that nano-hardness and elastic modulus of the films increase with increasing Ar concentration in the range of 17–50%, while decreases with increasing Ar concentration from 50% to 86%. The variations in the nano-hardness and the elastic modulus could be interpreted due to different  $sp^3$  fractions in the prepared *a*-C:H films. The variation of refractive index with wavelength have the same tendency for the *a*-C:H films prepared at different Ar concentrations, they decrease with increasing wavelength from 600 to 1700 nm. For certain wavelengths within 600–1700 nm, refractive index has the highest value at the Ar concentration of 50%, and it is smaller at the Ar concentration of 86% than at 17%. The results given above indicate that ratio of mixed gases has a strong influence on bonding configuration and properties of *a*-C:H films during deposition. The related mechanism is discussed in this paper.

**Keywords.** Amorphous hydrogenated carbon; middle frequency pulsed unbalanced magnetron sputtering technique;  $sp^3$  content; mechanical properties; refractive index.

## 1. Introduction

Amorphous hydrogenated carbon (*a*-C:H) films are metastable and in amorphous phase of carbon having  $sp^3$  and  $sp^2$  bonds with various amounts of hydrogen. *a*-C:H films have been investigated extensively due to their attractive properties including high hardness, low-friction coefficient, good wear-resistance, high optical transparency, high electrical resistivity, chemical inertness and biocompatibility (Clin *et al* 1999; Dai *et al* 2007; Kumari *et al* 2009). Therefore, they are widely used as hard transparent optical coatings, wear-resistant films in precision-machining, abrasion-resistant films in microelectronic–mechanical systems, low-*k* dielectric films in integrated circuits and biocompatible coatings (Clin *et al* 1999; Kumari *et al* 2009).

*a*-C:H films have been synthesized by a variety of methods for different applications such as plasma enhanced chemical vapour deposition, dielectric barrier discharge deposition, ion beam deposition, arc ion plating and magnetron sputtering etc (Robertson 2002; Zou *et al* 2004; Dey *et al* 2008). It is known that *a*-C:H is mainly composed of  $sp^3$  and  $sp^2$  and the properties of *a*-C:H films are strongly affected by

the ratio of  $sp^3/sp^2$ . It is found that the ratio of  $sp^3/sp^2$  is dependent on different deposition methods and their preparation parameters. For a certain preparation method, the ratio of  $sp^3/sp^2$  in films can be adjusted by adjusting one or two even three deposition parameters; consequently, film properties can also be controlled. Therefore, it is very important to look for some preparation parameters which can mainly control the ratio of  $sp^3/sp^2$  in the prepared *a*-C:H films. Much works have been performed on the relationship between film properties and deposition parameters (Robertson 2002; Zou *et al* 2004; Myung *et al* 2005; Dey *et al* 2008).

There are a lot of magnetron sputtering methods widely used for industrial applications due to their good reproducibility and controllability with large areas, high deposition rates and low deposition temperature. In our work, middle frequency pulsed unbalanced magnetron sputtering technique (MFPUMST) is used to deposit *a*-C:H films, such a method can effectively improve the adhesion of the coatings to substrate without adding substrate bias owing to the enhancement of the plasma density near the substrate (Dai *et al* 2009), and can significantly reduce arcs during film preparation due to pulsing the magnetron discharge, hence, improve quality of the deposited films (Huang *et al* 2006; Dai *et al* 2009).

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*a*-C:H film has a wide bandgap and its refractive index is variable by controlling the preparation parameters. Therefore, *a*-C:H film can be used as an antireflective protective surface layer matching infrared coatings for infrared windows. Such a *a*-C:H film should have a controlled refractive index as well as super mechanical properties. In this paper, one of deposition parameters, ratio of mixed gases, was changed to study its effects on bonding and properties of films deposited by MFPUMST.

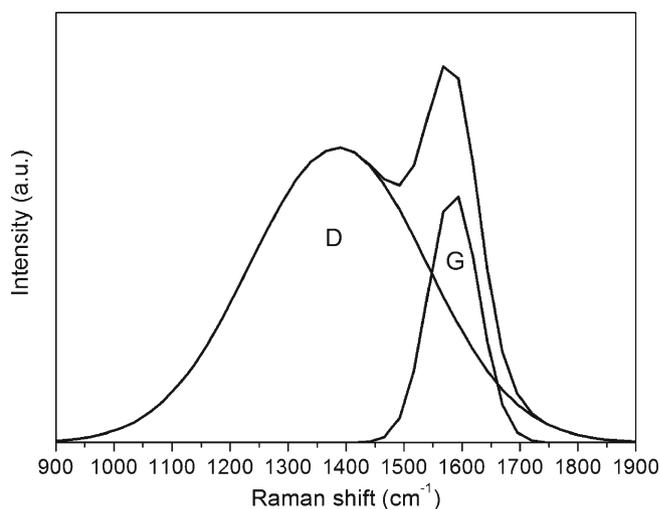
## 2. Experimental

A middle frequency pulsed unbalanced magnetron sputtering technique (MFPUMST) was used to deposit *a*-C:H films on Si (100) wafers with 40 kHz at 200 mA in a 80% duty factor. The silicon wafers as substrates were ultrasonically cleaned in acetone and ethanol for about 10 min, then rinsed in deionized water, and finally dried before installing in the vacuum chamber. The surface of the substrate was then bombarded by Ar plasma with 700 V bias voltage for more than 10 min to remove the surface contaminations prior to film deposition on it. Both Ar and CH<sub>4</sub> are with a purity of 99.99%, and the purity of graphite target is also 99.99%. A base pressure of  $5 \times 10^{-4}$  Pa in chamber was changed to  $4 \times 10^{-1}$  Pa due to putting Ar gas and then CH<sub>4</sub> gas into discharge chamber during film deposition. Samples were prepared at room temperature with 0 bias for 3 h, and the Ar concentration (Ar/Ar+CH<sub>4</sub>) in CH<sub>4</sub>-Ar mixture gases selected was 17%, 33%, 50%, 67% and 86%, respectively.

A RM2000 instrument by Renishaw, UK, with a 514.5 nm Ar<sup>+</sup> laser source was used for Raman spectral analysis. X-ray photoelectron spectroscopy (XPS) studies were carried out on the deposited films using a PHI Quantera SXM system with monochromatic Al K $\alpha$  radiation (1486.6 eV). A fully calibrated MTS Nano Indenter XP was used for nano-hardness and elastic modulus measurement of the films, all data of hardness and elastic modulus in the paper are obtained as an average value with 3 tested points. The refractive index of the films was determined by a M-2000DI spectroscopic ellipsometer (SE) in the wavelength range from 600 to 1700 nm.

## 3. Results and discussion

Raman spectroscopy is widely used to characterize structural quality of diamond, graphites, DLCs and carbon nanotubes, because of its sensitivity to changes in translation symmetry (Robertson 2002; Buijnsters *et al* 2006). The Raman spectra of *a*-C:H films consist of two peaks, the *G* peak around 1560 cm<sup>-1</sup> and the *D* peak around 1360 cm<sup>-1</sup>, for visible excitation (Robertson 2002; Buijnsters *et al* 2006; Dai *et al* 2007). The Raman spectra were deconvoluted with Gaussian curve fitting and the fitted parameters were used as the Raman parameters, including the peak position, bandwidth and spectra intensity. In fact, both *D* and *G* peaks are attributed to *sp*<sup>2</sup> bonding in the visible Raman spectra, the



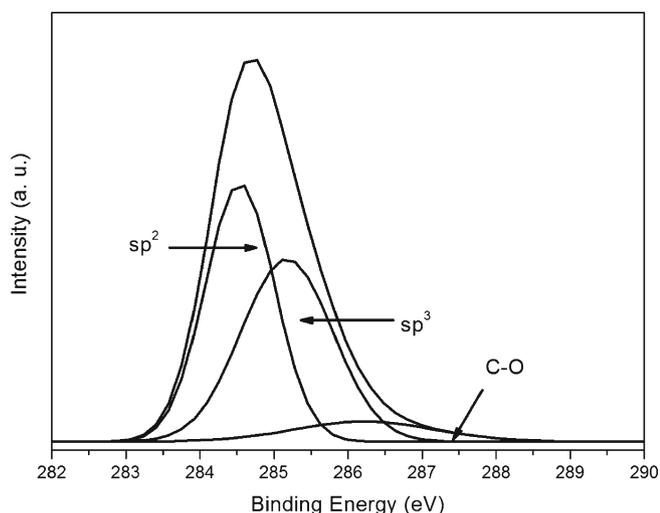
**Figure 1.** Raman spectrum of *a*-C:H film deposited at 17% Ar concentration.

**Table 1.** Bandwidth of *G* peak of *a*-C:H films deposited at different Ar concentrations.

Ar concentration (%)	17	33	50	67	86
Bandwidth of <i>G</i> peak (cm <sup>-1</sup> )	86.8	89.3	92.6	88.2	79.7

*D* peak is due to a breathing mode of those *sp*<sup>2</sup> sites only in rings, not in chains. The *G* peak is due to a stretching vibration of any pair of *sp*<sup>2</sup> sites, either in C=C chains or in aromatic rings. Thus, *G* peak does not only mean ‘graphite’ (Robertson 2002; Buijnsters *et al* 2006; Dai *et al* 2007). A new criteria for judging *sp*<sup>3</sup> fraction in the *a*-C:H films have been developed by us, in which the bandwidth of *G* peak can be used to measure *sp*<sup>3</sup> content, a wider bandwidth of *G* peak indicates a higher *sp*<sup>3</sup> fraction in the *a*-C:H films (Dai *et al* 2007).

Figure 1 shows Raman spectrum of *a*-C:H film prepared at a Ar concentration of 17%. The Raman spectrum decomposed by Gaussian fitting can be obtained as two peaks denoted as *G* and *D* at 1584 and 1388 cm<sup>-1</sup>, respectively. Similar spectra can be obtained for the *a*-C:H films deposited at other different Ar concentrations. The bandwidth of *G* peak with different Ar concentrations is shown in table 1. The bandwidth of *G* peak is 86.8 cm<sup>-1</sup> when the Ar concentration is 17%, it is 89.3 cm<sup>-1</sup> when the Ar concentration is 33%, it increases to 92.6 cm<sup>-1</sup> when the Ar concentration is 50%. Then it decreases to 88.2 cm<sup>-1</sup> when the Ar concentration is 67%, and it becomes 79.7 cm<sup>-1</sup> when the Ar concentration is 86%. These data seem to indicate that the bandwidth of *G* peak monotonously increases when the Ar concentration was in the range of 17–50%, and then monotonously decreases when the Ar concentration was in the range of 50–86%. It seems that the *sp*<sup>3</sup> fraction increases when the Ar concentration was in the range of 17–50%, and then decreases when the Ar concentration was in the range of 50–86%. Therefore,



**Figure 2.** Deconvolution of XPS  $C_{1s}$  peaks of  $a$ -C:H film deposited at 17% Ar concentration.

**Table 2.**  $sp^3/sp^2$  ratio based on XPS measurements for  $a$ -C:H films deposited at different Ar concentrations.

Ar concentration (%)	17	33	50	67	86
$sp^3/sp^2$	1.28	1.42	1.52	1.37	1.16

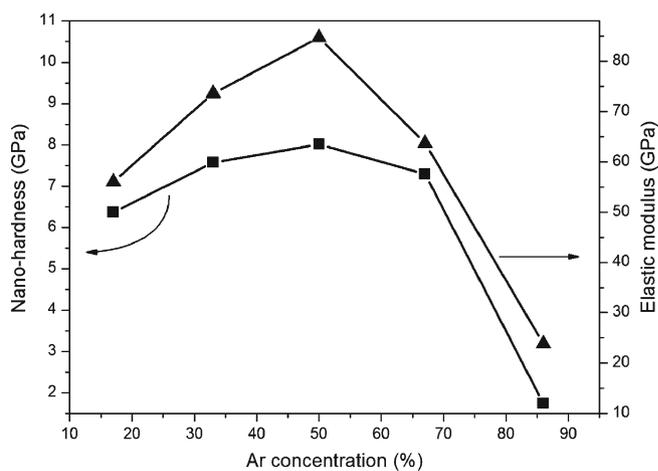
a highest  $sp^3$  content in the  $a$ -C:H films can be obtained at the Ar concentration around 50% during film deposition.

Raman spectroscopy is relatively unreliable in quantitative analysis of DLC films. To get quantitative results of film composition ( $sp^3:sp^2$ ), XPS analysis was employed. The deconvolution of XPS  $C_{1s}$  peaks of the  $a$ -C:H film prepared at a Ar concentration of 17% is shown in figure 2. One component at 284.5 eV corresponds to  $sp^2$  bond configuration, the second at 285.1 eV is due to  $sp^3$  bond one, and the third peak at 286.3 eV is attributed to C–O contamination due to the exposure of samples in air (Wang *et al* 2007). The ratio of  $sp^3/sp^2$  was determined by the ratio of the corresponding peak area (Wang *et al* 2007). Table 2 shows  $sp^3/sp^2$  ratio based on XPS measurements at different Ar concentrations. The  $sp^3/sp^2$  ratio is 1.28 when the Ar concentration is 17%, it is 1.42 at Ar concentration of 33%, it increases to 1.52 at Ar concentration of 50%. Then it decreases to 1.37 when Ar concentration is 67%, and it becomes 1.16 at the Ar concentration of 86%. This means that the  $sp^3$  fraction increases with increasing Ar concentration from 17% to 50%, then decreases with increasing Ar concentration from 50% to 86%. XPS result is consistent with that based on Raman measurement.

One of the most accepted models used to explain the deposition process of  $a$ -C:H films is the sub-plantation model which is suitable for carbon species with energy approximately from 10 to 1000 eV (Lifshitz 1996; Robertson 2002). When the energy of an impinging species ( $E_{im}$ ) is lower than the energy of penetration threshold ( $E_p$ ), i.e.  $E_{im} < E_p$ ,

such a species releases its energy via thermal spikes and just stick to the surface layers, and remain in their lowest energy state which is  $sp^2$  (Lifshitz 1996; Robertson 2002). When  $E_{im} > E_p$ , the carbonaceous species start penetrating the subsurface layers and get accommodated in the interstitial sites leading to an increase of the local density. The local bonding will then reform around that atom according to this new density, i.e. the local bonding tends to change to  $sp^3$  (Robertson 2002). However, when the energy of an impinging species are so high, they will cause increase of substrate temperature. In such a situation, carbonaceous species trapped in sub-surface area have to migrate to the top surface leading to the decrease in film density. Therefore, structure of film then changes from diamond-like carbon to graphite structure (Peng *et al* 2001; Robertson 2002; Chowdhury *et al* 2004). It has been found that the kinetic energy of argon ions is usually higher than hydrocarbon ions in the plasma of methane–argon gas (Liu *et al* 2006); the number of argon ions increases with increasing Ar concentration, the collision probability between Ar ions and hydrocarbon ions increases leading to more energy translated from argon ions to hydrocarbon ions, in other words, the kinetic energy of hydrocarbon ions increases with increasing Ar concentration (Chowdhury *et al* 2004). Based on the sub-plantation model, the fraction of carbonaceous species trapped in sub-surface area is increased with increasing Ar concentration from 17% to 50%, which causes increase in local density of the film; hence, fraction of  $sp^3$  component is increased. But, when Ar concentration further increases, energy of carbonaceous ions is also increased causing increase of substrate temperature leading to carbonaceous species trapped in sub-surface area to migrate to the surface, and local density of the film is then decreased causing a decrease in  $sp^3$  fraction. And this is also why  $sp^3$  fraction of the  $a$ -C:H film prepared at the Ar concentration of 86% is lower than that at 17%.

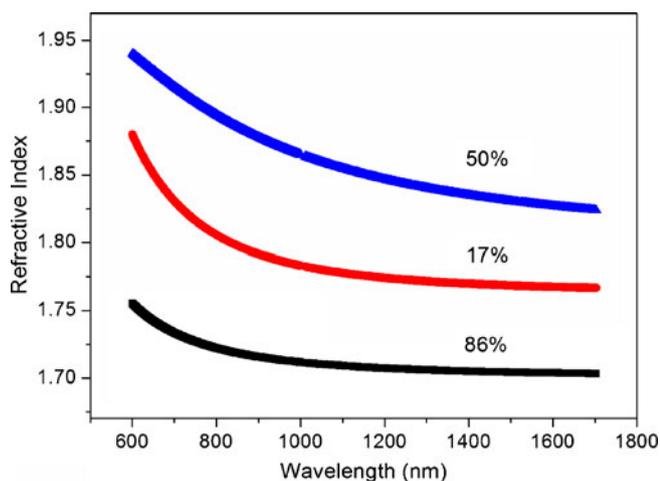
Nanoindentation technique is now widely used in evaluating the mechanical properties of thin and ultra-thin films.



**Figure 3.** Nano-hardness and elastic modulus of  $a$ -C:H films as a function of Ar concentration.

Figure 3 shows nano-hardness and elastic modulus of *a*-C:H films as a function of Ar concentration. The nano-hardness increases from 6.636 GPa at 17% Ar concentration to 8.014 GPa at 50% Ar concentration, however, further increase in Ar content results in a rapid decrease of nano-hardness. The elastic modulus also increases from 56.028 GPa at 17% Ar concentration to 84.678 GPa at 50% Ar concentration and then decreases to 23.835 GPa at 86% Ar concentration. The nano-hardness and elastic modulus of the *a*-C:H films have the same tendency, and the highest values of nano-hardness and elastic modulus were obtained from the *a*-C:H film deposited at 50% Ar concentration. Obviously, hardness and elastic modulus are dependent on the  $sp^3$  fraction in the *a*-C:H films, in other words, the higher  $sp^3$  fraction in the *a*-C:H films, the higher the hardness and elastic modulus (Robertson 2002; Dai et al 2007). According to the measured Raman and XPS results, highest  $sp^3$  fraction can be obtained for the *a*-C:H films deposited at a Ar concentration of 50%. Also, highest nano-hardness and highest elastic modulus values can be obtained for the *a*-C:H films deposited at Ar concentration of 50%.

Optical studies were carried out by spectroscopic ellipsometry (SE) over 600–1700 nm range. Figure 4 shows variation of refractive index with wavelength for the films deposited at different Ar concentrations. It can be found from figure 4 that the refractive index values depend on wavelength as well as Ar concentration. The refractive indexes have the same tendency for the *a*-C:H films prepared at different Ar concentrations, they decreased with increasing wavelength from 600 to 1700 nm, but they did not change when the wavelength was longer than 1200 nm. The refractive index of film deposited at 50% Ar concentration is between 1.940 and 1.824 over the range 600–1700 nm, and it is from 1.880 to 1.767 for the films deposited at 17% Ar concentration, while, it is between 1.755 and 1.703 at 86% Ar concentration. For certain wavelengths within 600–1700 nm,



**Figure 4.** Variation of refractive index with wavelength for films deposited under different Ar concentrations.

refractive index has the highest value at Ar concentration of 50%, and it is smaller at the Ar concentration of 86% than at 17%. According to the measured refractive index of the films deposited at different Ar concentrations, it can be deduced that film deposited at 50% Ar concentration is dense in comparison with those deposited at 17% and 86% Ar concentration (Dey et al 2008; Singh et al 2008). Based on the above analyses, it is concluded that the *a*-C:H films prepared by MFPUMST with a higher density have a higher refractive index, and also have more  $sp^3$  fractions.

#### 4. Conclusions

Amorphous hydrogenated carbon (*a*-C:H) films were synthesized by MFPUMST with a mixture of methane and argon as working gas. The effect of Ar concentration in the mixture gas on the bonds structure, mechanical properties and refractive index for such films was investigated.

(I) Raman and XPS spectra show that  $sp^3$  fraction in the *a*-C:H films increases with increasing Ar concentration from 17% to 50%, while it decreases with increasing Ar concentration from 50% to 86%. The effect of changes in Ar concentration on the  $sp^3$  fraction can be explained by the sub-plantation model.

(II) Nano-indentation measurements show that the nano-hardness and elastic modulus for the *a*-C:H films increase with increasing Ar concentration from 17% to 50%, while it decreases when Ar concentration is above 50%.

(III) Spectroscopic ellipsometry measurements show that the refractive index for the deposited *a*-C:H films at different Ar concentrations show the same tendency in the range of wavelength from 600 nm to 1700 nm. And for certain wavelength within 600–1700 nm, the refractive index has the highest value at a Ar concentration of 50%, and it is smaller at a Ar concentration of 86% than at 17%.

(IV) Based on the analyses shown here, the Ar concentration in the mixture of methane and argon gas plays an important role in the bonding structure, mechanical and optical properties of *a*-C:H films deposited by middle frequency pulsed unbalanced magnetron sputtering technique. It is concluded that the *a*-C:H films prepared by MFPUMST with a higher density have a higher refractive index, and also have more  $sp^3$  fraction.

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