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Effects of acetylene addition on mechanical and dielectric properties of amorphous carbon films

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Abstract

The para-xylene added with acetylene from 15% to 50% was plasma polymerized at 50 to 150 W to deposit the a-C:H films. After the films were annealed from 200 to 400 °C, the network structure, hardness and dielectric constant of films were analyzed by FT-IR, Raman, nanoindentor and capacitance–voltage plot, respectively. Those measured results suggest that hydrocarbon bonds and oxygen related bonds of the a-C:H film effectively reduce and the number of ordered aromatic rings increases with decreasing the deposition power after annealing at 400 °C. In addition, both the dielectric constant and the hardness, respectively, increase up to 2.82 and 2.37 GPa, but the adhesion strength decreases with increasing the C_2H_2 concentration and deposition power. Therefore, the a-C:H films not only have a lower dielectric constant, but also have enough mechanical strength for the IC processing.

Keywords: Acetylene; Plasma processing and deposition; Low dielectric constant

1. Introduction

Amorphous hydrogenated carbon (a-C:H) films have attracted intensive interests and investigations due to their outstanding characteristics, for example the chemical inertness, high hardness, high electrical resistance, low leakage current, low dielectric constant and flexible properties depending on deposition conditions [1,2]. On top of its unique properties, the dielectric constant is possibly as low as 2.6, which is influenced by the bonding element, structure and process [2,3]. Plasma-enhanced deposition is a proper process to control the energy and fluxes of ion bombardment on the surface of low *k* materials [4,5]. Thus, the plasma deposited a-C:H films could replace the traditional interlayer-metal dielectric (IMD), SiO_2, as a candidate for the next generation IMD.

For achieving the purpose of low *k* materials, both a lower induced polarization from sp^2 and sp^3 hybridized bonds in a-C:H films [6–8] and a higher porosity [9] can reduce the dielectric constant. Unfortunately, a-C:H films usually do not have enough mechanical strengths to resist the thermal budget and internal stress damage, inducing cracks and interface delaminations at the barrier/low *k* interface in the subsequent annealing and polishing processes [10,11]. Other low *k* materials also have similar problems in the mechanical strength with usual hardness value lower than 1 GPa [12–14]. For solving those problems, one possible solution is the addition of acetylene in plasma-enhanced deposition process to enhance the carbon precursor cross-linking by controlling the deposition power and acetylene concentration to raise the amount of higher strength bonds, for example C═C bond and aromatic structures [15]. It is expected that the acetylene addition could improve the hardness and the adhesion of a-C:H/Si interlayer. In fact, the electronic polarizations of carbon bonds are higher than that of hydrocarbon bonds, but that is a trade-off for achieving a lower dielectric constant while having higher bond strength [2].

In this study, we investigate the effects of the acetylene addition, deposition power and annealing treatment on the

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structure, dielectric and mechanical properties of the a-C:H films prepared with para-xylene in an argon plasma.

2. Experimental procedure

The a-C:H films were deposited by changing the deposition power and acetylene concentration in the parallel-plate radio-frequency plasma-enhanced chemical vapor deposited system. The para-xylene was heated in a bubbler system and carried by argon gas into the reactor. The p-type silicon and KBr disc were utilized as the substrates for preparing samples for Raman and Fourier transform infrared (FT-IR) spectroscopy, respectively. After the argon plasma treatment to remove the pollutants on these substrate surfaces, the precursor was carried by an argon gas into the reactor and the films were deposited at 1 Torr during all the deposition processes. The deposition power and acetylene addition were controlled from 50 to 150 W and 15% to 50%, respectively, to produce the a-C:H films, then the films were annealed from 200 to 400 °C in the N_2 atmosphere.

The structure of the a-C:H films was evaluated by Raman (LabRAM HR, Jobin Yvon.) and FT-IR (Spectrum One, Perkin Elmer Instruments) spectrometers. The hardness and the Young's modulus were determined by nanoindentor (Hysitron TroboScope). The indentation depths of each load were less than 1/10 of the film thickness for diminishing the substrate effect. The adhesion of the a-C:H films on the Si wafer was measured by pull-off test. The values of the hardness, Young's modulus and adhesion were obtained by averaging the measured results of 8 tests. The dielectric constants were determined from the capacitance–voltage (C–V) plot measured with the metal–insulator–semiconductor structure by the HP 4282 LCR meter at 1 MHz. In order to form the ohmic contact for the MIS structure, Al films were prepared by electron beam evaporation at a thickness of 300 nm both onto the a-C:H films as a circle of 3 μm in radius and onto the back side of the silicon substrates (Al/a-C:H/Si/Al).

3. Results and discussion

FT-IR spectroscope was utilized to investigate effects of the acetylene addition on the structure and polar group of the a-C:H films deposited with para-xylene as the precursor. Fig. 1 shows FT-IR spectra of the a-C:H film prepared at 150 W and 50% C_2H_2 after annealing from 200 to 400 °C. It shows that two significant peaks of the C–H stretching bands at 2960 and 2920 cm^{-1}, indicating the dominant anti-symmetric sp^2 CH_2 and sp^3 CH_2 stretching bands [16] respectively, are both clearly observed in all of the spectra, but the intensities dramatically reduce after annealing at 400 °C. It also could confirm the presence of aromatic structures by the sp^2 C–H stretching bands at 3050 cm^{-1} [17]. In contrast with hydrocarbon bonds, both of two peaks at 1610 and 1510 cm^{-1}, indicating the olefin and aromatic sp^2 C=C stretching bands respectively, are slightly influenced after the annealing treatment. According to the above results, peaks of the aromatic sp^2 C–H and aromatic C=C bonds show that the aromatic network of higher bond strength becomes a major structure after annealing due to the reduction of hydrocarbon bonds. Moreover, the sharp absorption band at about 1710 cm^{-1}, assigning to the C=O bonds, and the broad absorption bands from 3400 to 3550 cm^{-1}, indicating that the O–H stretching band [18], are also reduced after all of the annealing treatments. Frequently, the C=O and O–H bonds originate from the ambient contamination on the film surface and the incorporated impurities during film deposition, which results in the defects or dangling bonds with oxygen on the film surface [19] to start cracking or delaminating. Thus, the decrease of intensities of oxygen related bonds and hydrocarbon bonds after annealing represent effective reduction of film defects and weak bonds, which could improve the mechanical strength.

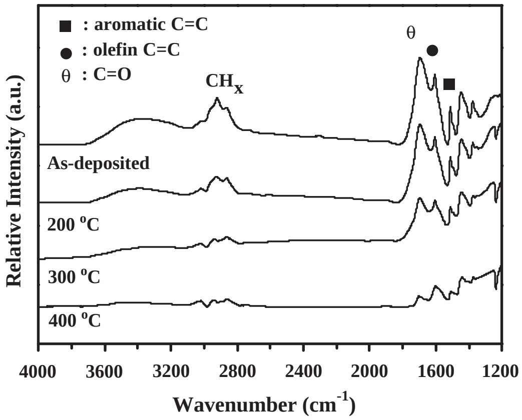

Fig. 1. FT-IR spectra of the a-C:H film deposited at 50% C_2H_2, 150 W after annealing from 200 to 400 °C.

Raman spectroscopy is another powerful tool to investigate the structure of a-C:H films. For quantitative analysis, Raman spectra were fitted to two Gaussian peaks denoting G and D band, respectively, located at 1590 and 1360 cm^{-1}. Fig. 2 shows the shift of G band position and I_D/I_G ratio of the a-C:H film prepared at the C_2H_2 concentration from 15% to 50% and deposition power from 50 to 150 W after annealing at 400 °C. According to Ferrari and Robertson's study [20], the G and D bands respectively locate near 1580 and 1360 cm^{-1}, originating from sp^2 sites only, where the G band is the bond stretching of all pairs of sp^2 atoms in both ring and chains and the D band is the breathing modes of aromatic structures. The shift of the G band indicates the increase in size and number of the sp^2 carbons, and the increase of the I_D/I_G ratio suggests an increase in the number of ordered aromatic rings [21]. It was found that the G band positions are almost fixed near 1590 cm^{-1} but the I_D/I_G ratio decreases with the deposition power,