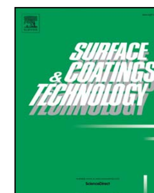
Surface & Coatings Technology 344 (2018) 12–20

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat



Hydrogen plasma-enhanced atomic layer deposition of hydrogenated amorphous carbon thin films

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ARTICLE INFO

Keywords:
Hydrogenated amorphous carbon
Atomic layer deposition
Hydrogen plasma
Carbon tetrabromide
Substrate pretreatment

ABSTRACT

Hydrogenated amorphous carbon (a-C:H) thin films were prepared by hydrogen plasma-enhanced atomic layer deposition (PE-ALD). The a-C:H thin films were grown at low temperatures in the range of 150–350 °C using CBr_4 as the precursor and hydrogen plasma as the reactant. Raman spectroscopy, secondary ion mass spectrometry, X-ray photoelectron spectroscopy and Fourier transform infrared measurements showed that the a-C:H films consist of hydrogenated nanocrystalline sp^3 diamond, disordered sp^3 carbon and sp^2-hybridized graphitic carbon incorporated with oxygen as a main contaminant. Moreover, the incorporation of bromine and oxygen in the a-C:H films was significantly reduced upon increasing the growth temperature from 200 to 300 °C. Surface hydroxylation and precursor exposure pretreatments were employed to saturate the adsorption of CBr_4 precursors and enhance the initial nucleation of carbon during the deposition of the a-C:H thin film by the PE-ALD process. In addition, the conformal growth of a-C:H thin films on three-dimensional structures was confirmed.

1. Introduction

Carbon is one of the most abundant elements in nature and is found in different forms in a variety of carbon materials, such as graphite (sp^2-hybridized carbon), diamond (sp^3-hybridized carbon), and amorphous carbon (a-C, with randomly sp^2- and sp^3-hybridized carbon). Each form has unique physical and chemical properties, depending on its structure [1,2]. Among the different forms, the disordered (a-C) one is particularly attractive, owing to its electrical properties, chemical inertness, and good hardness. The structure of a-C is stabilized by saturating dangling bonds with hydrogen, forming hydrogenated amorphous carbon (a-C:H), which has important advantages such as low cost and ease of synthesis, which make it an attractive material for practical applications such as lubricating coatings and double patterning hard-masks, and secondary (rechargeable) sodium-ion battery electrodes [3–6]. Nanocrystalline graphitic carbon, as a type of a-C, consists of nanosized sp^2 graphitic carbon domains which are attributed to better electrical conductivity than other types of a-C. For this reason, nanocrystalline graphitic carbon has been used as a coating material for transparent conducting films and lithium-ion batteries [7,8].

Conformal and uniform deposition of carbon materials on various substrate structures and materials becomes more and more important to many research areas. For example, with the current continuous decrease in the feature size of integrated circuits in the semiconductor industry, achieving a close control of the dimensions and high step coverage of hard mask spacers comprising a-C:H is a key requirement in order to fabricate uniform and conformal pattern features in self-aligned double patterning technologies [9]. In addition, the uniform and conformal coating process of thickness-controlled graphitic carbon layer on electrode materials is also important for rechargeable battery technologies, because graphitic carbon layer can improve the surface chemistry of the electrode materials, provide good conductivity, and protect the electrodes from direct contact with electrolytes [10].

A large number of studies have reported the deposition of carbon by chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques, such as filtered cathodic arc, microwave plasma-assisted, and pulsed laser deposition, as well as filament-assisted CVD, reactive particle beam assisted sputtering, and electrodeposition, among the others [11–16]. However, achieving the growth of uniform and conformal carbon films on high aspect ratio structures such as holes and trenches using those conventional deposition methods has been very challenging, owing to the low step coverage and high growth temperatures typical of these approaches.

Atomic layer deposition (ALD) is considered a promising technique for the fabrication of nanomaterials, as it enables the deposition of a thin film with good uniformity over a large area [17,18]. The key

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https://doi.org/10.1016/j.surfcoat.2018.02.082
Received 6 September 2017; Received in revised form 16 February 2018; Accepted 21 February 2018
Available online 02 March 2018
0257-8972/ © 2018 Published by Elsevier B.V.

advantages of the ALD technique include thickness control at the atomic scale, production of highly conformal films, and low-temperature growth [19]. Despite the high interest in carbon materials and the obvious potential of the ALD method for their preparation, there have been a few studies of the synthesis of any type of carbon using ALD. In 1993, Hukka et al. reported the atomic layer epitaxy (ALE) of diamond on a diamond (100) substrate by using chlorocarbon radicals and atomic hydrogen generated in a fluorine stream at a hot reactor [20]. In 1998, Komarov et al. also demonstrated the ALE of diamond films on Mo substrates using alternating fluxes of fluorocarbon radicals and atomic hydrogen generated in a hot filament reactor at high temperatures (over 700 °C) [21]. However, they did not achieve stable and reliable self-limiting growth for true ALD, and concluded that the growth process should be further optimized, for instance by investigating other halocarbon precursors and optimizing the ALD system. Recently, Zhang et al. demonstrated the ALD of graphene layers by using benzene precursor and hydrogen radical, showing layer-controlled and low temperature growth of high quality graphene by increasing ALD cycle [22]. However, the conformality of the graphene ALD on a nanostructure was not discussed, and the substrate material was limited to the copper foil as a growth catalyst.

The hydrogen plasma-enhanced ALD (PE-ALD) is a useful technique for the deposition of single-element films, especially at low deposition temperatures [23,24]. For example, hydrogen PE-ALD of semiconductors (Si and Ge) and metals (Ti, Cu, Ta, Ag, and Pd) has been performed using halide precursors, because of their high chemical reactivity with atomic hydrogen at low temperatures [25–31]. This same strategy should also enable the fabrication of carbon by PE-ALD using carbon halide precursors and atomic hydrogen: this would represent a very interesting approach with various potential applications. Among the possible carbon halide precursors, CBr_4 has a lower bond dissociation energy (approximately 234 kJ·mol^{-1} for the C−Br bond) compared with other halocarbon precursors (approximately 519 kJ·mol^{-1} for C−F bonds in CF_4 and 297 kJ·mol^{-1} for C−Cl bonds in CCl_4) and even aliphatic hydrocarbon precursors [32–35]. Furthermore, the good controllability and stability of the CBr_4 vapor flux near room temperature are also beneficial for ensuring a homogeneous supply of carbon [36]. For these reasons, CBr_4 has been frequently employed as a C dopant precursor to prepare compound semiconductors such as GaAs by molecular beam epitaxy [37,38]. Moreover, the bromocarbon molecules (CBr_4 or $CHBr_3$) are subsequently decomposed to bromomethyl radicals and HBr byproducts under atomic hydrogen, which highlights their relatively high reactivity with atomic hydrogen at low temperatures [32,37,39].

In this study, we report the growth of a-C:H thin films on a hydroxylated SiO_2 substrate by PE-ALD using CBr_4 and hydrogen plasma. Various experimental conditions, including substrate surface pretreatment, substrate temperature, and precursor injection time, were optimized to achieve self-limited ALD growth and excellent conformality of the a-C:H films. The thickness of the deposited a-C:H film was measured by spectroscopic ellipsometry and field-emission scanning electron microscopy (FE-SEM). The nanoscale surface profile of the a-C:H films were observed by an atomic force microscopy (AFM), whereas their chemical characterizations were performed by X-ray photoemission spectroscopy (XPS), secondary ion mass spectrometry (SIMS), Fourier transform infrared (FT-IR) spectroscopy and Raman spectroscopy. Also the electrical properties, such as field-effect mobility (μ_{eff}) and sheet resistance, were evaluated by the fabrication of back-gated a-C:H thin film transistors (C-TFTs).

2. Experimental

2.1. Experimental setup

The PE-ALD chamber used for depositing the a-C:H thin film consists of a showerhead-type injector and a capacitively coupled plasma (CCP) reactor with a 13.56 MHz radio frequency (rf) generator. The sample stage in the center of the chamber is heated up to 400 °C (calibrated to the substrate temperature, T_s) and pumped down to a low vacuum of ~10^{-1} Pa. The CBr_4 precursor (99%, Sigma-Aldrich) was vaporized at room temperature. The supply line must be continuously heated at a relatively high temperature of ~70 °C to maintain a good CBr_4 flux stability and avoid CBr_4 condensation. The CBr_4 exposure pressure was maintained at 1.3 Pa. The flow rates of Ar purging gas and H_2 reactant gas (of 99.9999% purity) were kept constant by using mass flow controllers. T_s was changed from 150 to 400 °C for assessing the effect of growth temperature on the PE-ALD growth characteristics and film properties. However, in order to study the self-limiting growth *via* saturation of the precursor exposure time (t_s), T_s was fixed at 300 °C.

2.2. Substrate pretreatments

SiO_2 layers (of 285 nm thickness) thermally grown on p-Si(100) wafers were cleaned with acetone, ethanol, and de-ionized water prior to deposition in an ultrasonic bath. Prior to the PE-ALD process, the SiO_2 substrate was hydroxylated by *in-situ* O_2 plasma pretreatment using the CCP reactor (generated power of 200 W) along with high-purity O_2 gas (99.9999%) at a fixed flow rate of 200 sccm for 30 s. The O_2 plasma pretreatment is frequently used to oxidize the surface intermediates and produce hydroxyl groups before the deposition of the subsequent layer [40]. This hydroxylation of Si by using O_2 plasma can be achieved when the oxygen plasma is contaminated with dissociated desorbed H_2O and hydrocarbons which can come from the low vacuum condition (~0.1 Pa) of the ALD chamber and the desorption and outgassing of the chamber wall with plasma surface interaction. Due to the plasma induced surface charge, the O_2 plasma treatment for a short period (tens of seconds) activates more of the −OH groups on the SiO_2 surface, which improves the subsequent adsorption with the precursor molecules [41]. The *in-situ* O_2 plasma treatment was carried out following the CBr_4 exposure pretreatment.

2.3. PE-ALD synthesis of a-C:H films

Each PE-ALD cycle consists of four sequential steps: exposure of CBr_4 to the hydroxylated SiO_2 substrate for a t_s of 4, 6, 8, 10, 14, and 18 s (step 1), purging of residual precursor molecules by inert Ar gas (step 2), exposure to hydrogen plasma gas (with a rf power of 200 W) at a partial pressure of ~10^2 Pa for a plasma pulse time (t_p) of 1.5 s (step 3), and purging of byproducts and residual H_2 reactant gas using inert Ar gas (step 4). The Ar purging gas was maintained at a fixed flow rate of 90 sccm for 8 s.

2.4. Characterization of PE-ALD a-C:H films

In order to determine the growth rates and conformality, the thickness of the deposited a-C:H film was measured using spectroscopic ellipsometry (Ellipso Technology, Elli-Se-F, λ = 380–1030 nm) and cross-sectional FE-SEM (JEOL JSM-6700F). The cross-sectional microstructure of the a-C:H film was also observed by high-resolution transmission electron microscopy (HR-TEM, Tecnai F20, FEI) with a 200 keV electron beam. For the TEM measurement, to distinguish the a-C:H film from the carbon epoxy layer, we coated a glue layer of Pt on the a-C:H film. The nanoscale surface profile of the deposited a-C:H thin film was examined by AFM (Multimode, VEECO). Raman spectroscopic measurements (Jobin Yvon, Aramis, with an Ar-ion laser excitation wavelength of 532 nm and a laser beam size of 1 μm^2) were carried out to analyze the structural arrangement of carbon atoms.

XPS measurements (ESCALab 220i-XL) of the a-C:H films were performed using a monochromatic X-ray source (Al K_α radiation, photon energy 1486.6 eV and analysis area: 100 μm^2), following surface cleaning by Ar^+ ion bombardment (energy: 3 keV; beam current density: 22.2 mA/cm^2; induced beam current: 2 mA; rastered over a

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