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Humidity resistant hydrogenated carbon nitride films

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ABSTRACT

The aim of this study is to prepare the hydrogenated carbon nitrides films which possess good adhesion to silicon substrates and stability in humid surroundings. The films were prepared by magnetron sputtering from pure graphite target in a nitrogen-hydrogen discharge. Two main factors can lead to delamination of the films. The first is the high value of residual stress and the second is the absorption of moisture into the bulk and their affect on films/substrates interface. Both factors were eliminated by adding hydrogen and post-deposition annealing in the vacuum. The influence of annealing (to 200, 400, 600, 800 and 1000 °C) on chemical composition and microstructure was studied by various methods. For preparation of humidity (water) resistant films we have added 15% partial pressure of hydrogen to nitrogen discharge and annealed the samples in vacuum to minimum temperature, which was 600 °C. The heating to 600 °C causes the increasing of carbon – nitride ratio from 2.0 to 2.4 and the relative atomic concentration calculated from XPS data (N 1s peak areas of C—N and C=N) reveals that amount of C—N bonds increases from 49% to 57%. Desorption of absorbed moistures and elements from the film was studied by Thermal Desorption Spectroscopy. Dominant molecules in TDS spectra were HCN and N_2, which were correlated with changes in chemical composition, measured by Rutherford Backscattering Spectroscopy and Elastic Recoil Detection Analysis. For observation of films delamination caused by high compressive stress, the Scanning Low Energy Electron Microscopy was used.

1. Introduction

Amy Liu and Marvin Cohen predicted the material β-C_3N_4 with hardness greater than a diamond [1]. Since this study, the carbon nitrides have been studied very intensively due to their perspective mechanical properties. Other promising properties were discovered over time and now these films are used as protection coatings in various applications. The newest research papers present the carbon nitride films as possible candidates to anticorrosion protection layers [2,3], electrodes in electrochemical sensors and gas sensors [4–6]. One of the key issues preventing the wider use of these films is the residual stress restricting the preparation of stable layers with thickness higher than few nanometers. Basically, two different types of stress can be identified in thin films: compressive stress and tensile stress. Compressive stress can lead to wrinkling and film delamination, and tensile stress can cause the fracturing of thin films [7,8]. Generally, we can reduce the stress by modifying the magnetron sputtering deposition process (gas pressure, substrate bias, temperature, angle of deposition, cathode power, etc.) or we can change the composition of the reactive gas or targets [7]. For reactions sputtering preparation of films from a graphite target in nitrogen discharge a solution is to add a specific quantity of hydrogen [9,10]. Carbon nitrides with and without hydrogen were compared in detail in our previous paper [10]. When we decreased the high value of compressive residual stress, the films with hydrogen had a good quality without buckling and telephone cords (compressive stress). But during WCA (Water Contact Angle) experiments we discovered the destruction of CN_x:H film (delamination blisters on all sample surfaces) in a moment. This effect is caused by absorption of moisture, its diffusion into the bulk, and then to the interface [11–13]. From practical point of view, the using of these films in a real environment is impossible for a long time. The post-deposition annealing in vacuum can be a way to improve adhesion between interfaces and eliminated the absorption character of the films, but the properties of the film can be changed greatly. A very detailed study about the annealing of carbon nitride films was published by W. Xu et al. [14] and M. Lejeune

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et al. [15]. The aim of this paper is to show a way of preparing the hydrogenated carbon nitrides with good adhesion and resistance to humidity.

2. Experiment

The films were prepared at room temperature from the graphite target of high purity (99.9999%) in a nitrogen/hydrogen discharge in a commercially available Z 550 RF magnetron sputtering plant (Leybold Heraeus). The partial pressure of hydrogen in nitrogen was systematically changed from 0% to 20% and total pressure of gases was 0.2 Pa. During the deposition, the power was 500 W. As a substrate we used (0 0 1) oriented silicon, cleaned in an acetone bath in ultrasound. The evacuation system consists of a rotary and turbomoleculary pump, limited pressure is 10^{-4} Pa.

In order to determine stress in thin films we used a home assembled high-resolution X-ray diffractometer. The apparatus is equipped with a conventional Cu X-ray tube and a four-bounce Ge 220 monochromator. The stress in the layer bends also the used silicon substrate. The curvature radius of substrate was determined from the shift of the 004 diffraction maximum at selected points on the samples and calculated by Stoney's equation. The use of Stoney's equation is limited by the criterions described in [16].

For observation of microstructure and the consequences of compressive stress to the films, we used Scanning Low Energy Electron Microscopy (SLEEM). SLEEM is increasingly becoming recognized as a valuable analytical tool in the field of materials science [17,18]. Experiments were made in the Tescan TS 5130 MM and high resolution scanning (transmission) electron microscope Magellan 400L. Both devices are equipped with the Cathode Lens system (CL), which enable us to observe samples at arbitrary landing energies of the illuminating electrons. A negatively biased specimen forms the cathode and the earthed scintillation detector forms the anode of the CL. A detected signal is created by secondary electrons and back scattering electrons together (secondary electrons usually give information about topography, while back scattering electron give information about materials contrasts and crystallography [19]). The Operation of a S(T)EM at low energies offers several advantages: an increase of signal, given by SE and therefore high signal to noise ratio of the final image, smaller interaction volume and elimination of charging effects [18].

Desorption of absorbed moistures from the films and interfaces has been investigated by means of Thermal Desorption Spectroscopy aperture (TDS), where the samples were annealed in a quartz chamber pumped down to pressure of 10^{-5} Pa and desorption masses were detected by quadrupole mass analyzer. The temperature in the chamber was increased up to the final temperature at the rate of 10 °C/min. TDS measurement is the appropriate technique to probe: the presence of voids, the contaminant species and the stability of the local microstructure as a function of the annealing temperature [20].

Several properties change during annealing; we have focused on thickness, chemical composition, microstructure and wettability. The elemental composition of the films was determined by Rutherford Back-Scattering spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) methods using a Van de Graaf generator with a linear electrostatic accelerator. The contents of carbon, nitrogen and oxygen were measured by RBS using 1.74 MeV, 2.30 MeV and 2.70 MeV protons and 3.04 MeV alpha particles as projectiles. The hydrogen was measured by ERDA with an incident beam of 2.75 MeV alpha particles at a 75° angle to the normal sample surface. The hydrogen atoms recoiled under the angle of 30° were detected with a surface barrier detector covered by a 12 μm thick mylar stopping foil. The RBS and ERDA measurements were evaluated by computer codes GISA 3 [21] and SIMNRA [22], using enhanced non-Rutherford cross-section values from a SigmaBase (also part of SIMNRA Code).

XPS analysis was performed in a UHV chamber, using a commercial instrument (Omicron DAR400 X-ray source and EA125 electron spectrometer). All the measurements were carried out at room temperature using X-ray Al Kα radiation and the pressure during the measurement was better than 7×10^{-7} Pa. An emission angle of 50° was used (measured from the surface normal).

For many applications is necessary to know the wettability of surfaces. We have tested Water Contact Angle (WCA) on the commerciall device SEE System by Advex Instruments, which enables us to calculate the WCA. The measurement of thickness was realized by profilometer Talystep, and a Fischerscope H100 depth sensing indentation tester equipped with a Berkovich tip was used to measure films indentation hardness (HIT).

3. Results

For studying films surfaces, SEM is usually used. Although this method needs a vacuum, the analysis is relatively fast. In commercial SEM, the primary electron energy usually uses 10 keV and higher voltage. At this energy, the information comes from a bigger volume and due to that, more information about the surface is distorted from a signal of substrates, which makes the observation of details impossible. The next problem of non-conductor materials is an accumulating of charge on the surface during observation in SEM and the so-called edge effect. These problems can be solved by using a lower energy of incident electron (Fig. 1). In our case we have used SEM equipped with cathode lens (CL) mode.

For an observation of the next images of films, we used the impact energy of primary electron 2 keV, where it is possible to observe the details and eliminated the charging effect.

As was written in the introduction, the two main factors that lead to delamination of carbon nitrides on silicon substrates are the high value of compressive stress and the absorption of moisture. The first has been eliminated by hydrogen. The optimal ratio of hydrogen and nitrogen was 15% [10]. The results are shown in Fig. 2. In the graph we can observe the dependence of deposition rate and residual stress to quantity of hydrogen in nitrogen discharge. Good result is observed by the lowest residual stress, the deposition rate is the highest, which is very important for industry application.

After 30 days (the samples were outside the vacuum chamber) we made images by SLEEM and observed the delamination in the case of samples to 10% partial pressure of hydrogen in nitrogen discharge. The results are shown in Fig. 3. The films had a thickness about 200 nm, and with decreasing stress the "telephone cords" were discovered sporadically (10% partial pressure of H). The films from 15% partial pressure of H are without defects, but the contact with water caused total destruction after few seconds, which was discovered later.

For next study we have chosen a sample with 15% partial pressure of hydrogen in nitrogen (the sample will be later labeled CN_x:H). The influence of water to films have been discovered when we started to analyze the Water Contact Angle (WCA). After a post-deposition annealing in vacuum (10^{-5} Pa, heating rate 10 °C/min to final temperature) of CN_x:H to (200, 400, 600, 800 and 1000) °C we conducted the WCA test. The results of that test are in Fig. 4.

Before WCA test, the samples were without any deformation. The delamination and cracking started after contact with demineralized water (in the case of sample without annealing, 200 °C and