Surface & Coatings Technology 204 (2010) 3234–3237

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Surface characterization and properties of silicon nitride films prepared by ion-assisted deposition

Shih-Liang Ku *, Cheng-Chung Lee

Department of Optics and Photonics, National Central University, Chung-Li, 320, Taiwan

ARTICLE INFO

Article history:
Received 3 November 2009
Accepted in revised form 11 March 2010
Available online 19 March 2010

Keywords:
Silicon nitride
IAD
Surface morphology
Composition
Mechanical property
Infrared optical constants

ABSTRACT

Silicon nitride (SiN) films had been prepared at low substrate temperature (100 °C) using the ion-assisted deposition (IAD) process. The films had been analyzed by the measurement of X-ray diffraction, atomic force microscopy, Fourier transform infrared spectrometry, nano indenter, and ellipsometry. The effects of N-ion current density on the surface morphology, compositional, mechanical, and infrared optical properties of SiN thin films were investigated. The results showed that the stoichiometric Si_3N_4 thin film with desirable properties, such as continuous and smooth surface morphology, extremely low hydrogen content, mechanical strong, and low extinction coefficient, could be obtained by using the IAD technique.

1. Introduction

Silicon nitride (SiN) films are widely used in optical and microelectronic devices due to their excellent optical, chemical, and mechanical properties. In recent years, there has been renewed interest in the application of SiN film in the infrared (IR) interference coating [1–3]. SiN films are conventionally prepared by chemical vapor deposition (CVD) method, with or without plasma assist. Although a high deposition rate can be obtained, the main disadvantage of CVD method is the high substrate temperature and the significant incorporation of hydrogen in the SiN films [4–6]. The high substrate temperature is not generally desired in many device applications and the hydrogen in the film causes the degradation of the properties of SiN. To get hydrogen-free and low temperature SiN films, many studies have focused on physical vapor deposition (PVD) methods, such as magnetron sputtering [7–10] and dual ion beam sputtering [11–13]. However, the shortcoming of the sputtering method is its relatively low deposition rate for the industrial production.

Due to the high flexibility, adaptability to lots of materials used in the optical thin film, thermal evaporation, which can obtain the high deposition rate, is the most widely used PVD process in thin film fabrication. However, SiN does not chemisorb the molecular nitrogen. Thus, it is impossible to obtain the stoichiometric Si_3N_4 film by reactive evaporation in nitrogen atmosphere [14]. Ion-assisted deposition (IAD) is a well-known method with a positive effect on the optical and structural properties of thin films. Thin films prepared by ion-assisted thermal evaporation not only keeps the flexibility of thermal evaporation, but also has the advantages of ion-based process.

In the work, amorphous SiN films were prepared by the IAD process. The effects of N-ion current density on the surface morphology, chemical bonding configurations, composition, nano hardness, and infrared optical constants were primarily investigated.

2. Experiments

2.1. Film deposition

An Optorun OTFC-1100 series (Optorun Co.,) coating system, which is equipped with a 17 cm radio-frequency ion source (Optorun Co., OIS-One), was used to deposit the films. Depending on the experimental purpose, the BK7 glass, and N-type <100> silicon wafer were used as substrates. These substrates were first cleaned by a standard procedure to remove surface contaminant, followed by argon ion bombardment (800 eV, 60 μA/cm^2) for 5 min, prior to the deposition. The SiN source material (99.99% purity, Opetech Materials Co.) was evaporated by an electron beam gun. The deposition chamber was evacuated by a cryo-pump to a base pressure of less than 1×10^{-4} Pa. The chamber pressure rose when starting to evaporate the material. The working pressure was 6×10^{-3} Pa in the non-IAD process. During the IAD process, high-purity nitrogen gas (99.9995%) was used as the working gas. This nitrogen gas also fed in to the chamber, and the operating pressure was maintained at

* Corresponding author.
E-mail address: slku@dop.ncu.edu.tw (S.-L. Ku).

0257-8972/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2010.03.022

2.6×10^{-2} Pa by an automatic pressure control unit. The ion energy was 600 eV, and the current density (J) was varied from 10 μA/cm^2 to 56 μA/cm^2. The J was detected at the position in which the substrate was placed by a commercial measuring program (Optorun Co., OIS-CDMP X30). The deposition rate, which was controlled by a quartz-crystal monitor (Inficon Co., IC/5), was about 18 nm/min. The final thickness of the film was in the region from 258 nm to 279 nm. The substrate was heated to 100 °C during deposition.

2.2. Film characterization

The crystalline structure of the films deposition on BK7 glass was investigated using X-ray diffractometer (XRD, Bruker Axe D8). Surface morphology and the roughness of the films deposition on silicon wafer were measured by atomic force microscopy (AFM, Veeco Dimension 3100) in the contact mode. The value of root-mean-square (rms) surface roughness was evaluated.

In order to analyze the chemical state of the films, the IR absorption spectra of the films deposited on the silicon wafer were obtained by a Fourier transform infrared (FTIR) spectrophotometer (Bomem MB-100) in the range of 4000–500 cm^{-1}. The resolution was 4 cm^{-1} during the measurement.

The hardness and Young's modulus of the films deposited on Si wafer were obtained using the nano indenter system (MTS Nano Indenter XP). To avoid the interference from the silicon wafer substrate, the indentations were made within a depth of approximately 1/10 – 1/5 of the film thickness.

The thickness and the IR optical constants of the SiN thin films deposited on the silicon wafer were determined by an infrared variable angle spectroscopic ellipsometer (IR-VASE, J.A. Woollam Co.) at room temperature. Each film was measured at two different incident angles, and the resultant data were analyzed using the WVASE32 software version 3.686 developed by the J.A. Woollam Co.

3. Results and discussion

3.1. Microstructure and surface morphology

All films were inspected by XRD, and no X-ray diffraction peak was found in the resultant spectra. This result indicated that all the films were amorphous.

AFM studies were carried out in order to investigate the surface morphology and the roughness of the films. All the film had been scanned on two surface areas to check the consistency of the images. The sampling area was 5×5 μm^2. Fig. 1(a)–(c) shows the three-dimensional AFM images of films deposited on silicon wafer with $J=0$, 20, and 50 μA/cm^2, respectively. As it can be seen in Fig. 1(a), the non-IAD film showed surface morphology with projections exhibiting columnar growth. This surface morphology was attributed to the films had the columnar growth, which has been confirmed by SEM measurement in a previous stage of this work [15]. On the other hand, as seen in Fig. 1(b), the surface irregularities became remarkable smaller with N-ion bombardment during the film growth.

As shown in Fig. 1(c), a homogeneous, continuous and smooth morphology was obtained in the film deposited at $J=50$ μA/cm^2. The rms surface roughness of the films was evaluated. Fig. 2 shows the variation of the surface roughness of the films as a function of J. The surface roughness of the films was drastically reduced from 1.72 nm to 0.42 nm as J increased. Previous studies [16,17] had reported that these surface features are directly relate to columnar structure surrounded by voids. Similar result had been observed for SiN films prepared by reactive bias magnetron sputtering [7,18]. Kim et al. [7] had concluded that the bombardment-induced mobility of the depositing adatoms increased with increasing bias voltage, leading to the transition of the microstructure from the open columnar structure to a denser, smoother film structure. As confirmed by SEM

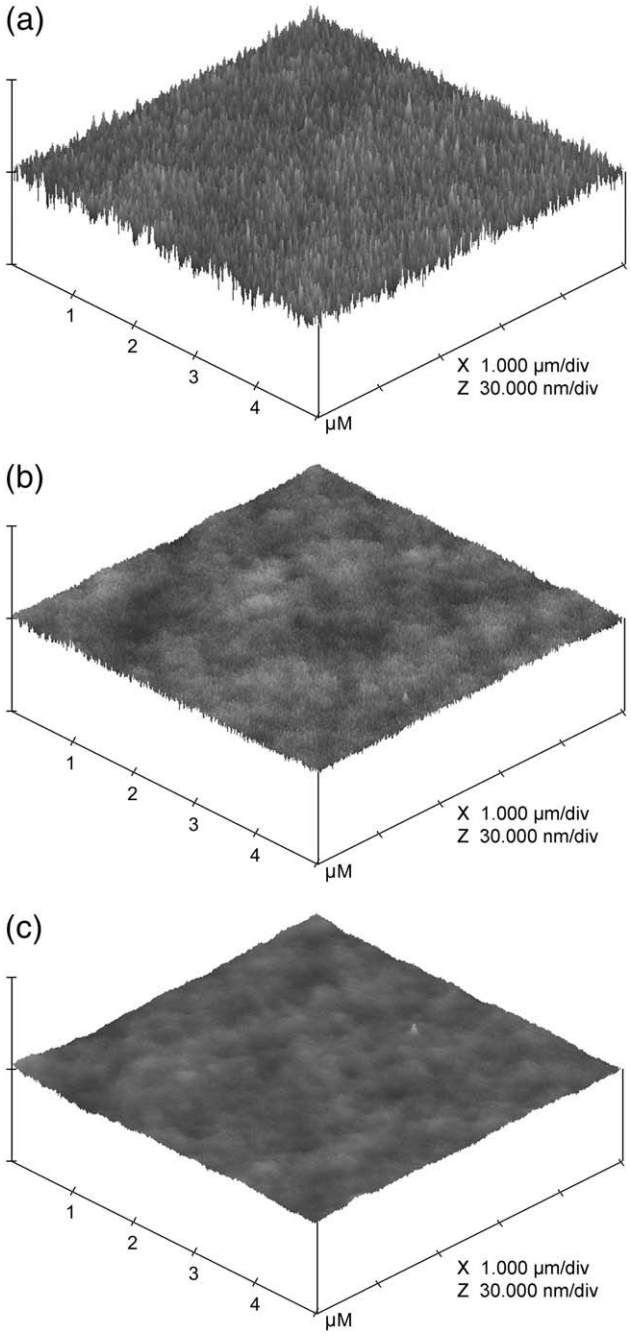

Fig. 1. AFM micrographs of the films deposited at (a) $J=0$ μA/cm^2 (non-IAD film), (b) $J=20$ μA/cm^2, and (c) $J=50$ μA/cm^2.

study in a previous report [15], N-ions bombardment minimized or removed the intercolumnar network of voids or low density regions, and resulted in a progressive refinement of the microstructure of film. Therefore, the variation of surface morphology in our study was attributed to the increased atatom mobility, which was caused by the N-ion bombardment during the film growth.

3.2. Compositional properties

The chemical bonding configurations of the as-deposited SiN films can be verified by FTIR measurement [5,7,9,11,19–23]. The infrared absorbance spectra were measured in the range of 4000–500 cm^{-1} and corrected for bare silicon wafer absorbance. Each spectrum was an