Materials Science in Semiconductor Processing 89 (2019) 1–5

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Low atomic number silicon nitride films for transmission electron microscopy

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ARTICLE INFO

Keywords:
TEM imaging
Resolution
Silicon nitride
Atomic number
Stress

ABSTRACT

Low stress silicon (Si)-rich silicon nitride (SiN_x) films are usually used as membranes of microcapsules for transmission electron microscopy (TEM). Their relatively high atomic number has a negative impact on resolution, which is a key factor that affects imaging performance. To improve resolution, reducing Si content in films is an effective approach. However, the non-Si-rich SiN_x films have large tensile stress and are ease to crack. In this study, ion implantation is utilized to adjust the stress of nearly stoichiometric (NS) SiN_x films. The effects of ion implantation and thermal annealing on film properties are carefully analyzed. It is found that the NS SiN_x films implanted with nitrogen (N) and annealed at low anneal temperature have both low atomic number and low stress, and their properties are very close to low stress Si-rich SiN_x films. Moreover, a simple microcapsule is fabricated using the low atomic number SiN_x films, and performs a TEM observation of water-soluble polypeptides growth. Polypeptides much smaller than 100 nm in size are observed.

1. Introduction

Transmission electron microscopy (TEM) is a powerful tool for imaging and characterizing materials at high resolution. It has been widely used in nanoscience and nanotechnology, including material synthesis [1], energy conversion [2], and life science [3].

Samples that analyzed in TEM should be stable in the vacuum environment. The use of microcapsules enables us to examine not only solid, but also liquid and gas [4–6]. The microcapsules are composed of two counterparts that contain membranes. The membranes separate the liquid or gas from the vacuum, while confine it into a layer for imaging.

There is a main limitation of the microcapsules, the membranes would scatter the imaging electrons and reduce the resolution. Low atomic number materials are beneficial for electron transparency. Recently, carbon foils, graphene sheets, and graphene oxide monolayers have been explored as membranes [7–9]. However, low stress silicon nitride (SiN_x) films are increasingly popular, as they are easily manufactured and have remarkable advantages in mechanical properties and chemical stability [10–12].

Until now the low stress SiN_x films are all rich of silicon (Si) [13]. This is because tensile stress is caused by the conformation of stable Si-nitrogen (N) bonds during the film deposition [14]. Si-rich SiN_x films have less Si–N bonds; hence, they can obtain a less tensile stress. It is also worth noting that the excessive Si makes the films have relatively high atomic number, for Si has higher atomic number than N.

To overcome this shortage, great efforts have put into reducing the film thickness to improve resolution. The films thickness has been decreased from 100 to 20 nm [15,16], but it is difficult to make a further reduction. This is due to the fact that thinner films would greatly bow under vacuum, and even could not withstand the pressure difference.

Another approach is to reduce the film atomic number. Previous works have revealed that the SiN_x films with different Si contents can be obtained by adjusting the deposition parameters [17,18]. However, large tensile stress, which will induce films to crack, exists in non-Si-rich SiN_x films. Ion implantation is an effective method to adjust the stress in films by atomic collisions [19,20], and yet its influence on film properties such as chemistry composition, structural characterization, mechanical properties and chemical stability hasn't been studied.

In this work, the method for preparation of low atomic number SiN_x films for TEM is systematically investigated. The relationship between atomic number and N/Si ratio in SiN_x films, as well as the relation of resolution to atomic number are firstly discussed. Then, nearly stoichiometric (NS) SiN_x films are deposited, and the effects of ion implantation and thermal annealing on film properties are carefully

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https://doi.org/10.1016/j.mssp.2018.08.024
Received 18 July 2018; Received in revised form 21 August 2018; Accepted 22 August 2018

analyzed. Finally, a microcapsule, which is based on the low atomic number SiN_x films, is fabricated and used for TEM imaging.

2. Theory

The atomic number of SiN_x films, which N/Si ratio is x, can be expressed as:

$$Z = \left(\frac{1}{1+x} \times 14^2 + \frac{x}{1+x} \times 7^2\right)^{1/2} \tag{1}$$

In TEM imaging, beam broadening and chromatic aberrations are two critical factors that govern resolution, that is:

$$r = r_b + r_c \tag{2}$$

Beam broadening of a coherent electron beam is caused by elastic scattering of electrons and defined as [21]:

$$r_b = 6.21 \times 10^3 \frac{Z}{E_0}\left(\frac{\rho}{W}\right)^{\frac{1}{2}} t^{\frac{3}{2}} \tag{3}$$

where E_0 is the beam energy; ρ, t and W are the density, thickness and atomic weight of SiN_x films, respectively.

Chromatic aberration, on the other hand, is a result of inelastic scattering of electrons and can be given by [22]:

$$r_c = C_c \beta \frac{\Delta E}{E_0} \tag{4}$$

where C_c is the chromatic aberration coefficient, β is the objective semi-angle, and ΔE is the energy loss by electron due to an inelastic scattering, there is [23]:

$$\Delta E = \frac{N_A e^4 Z \rho t}{2\pi \varepsilon_0^2 W E_0} \tag{5}$$

here, N_A is Avogadro's number, e is the elementary charge, ε_0 is the permittivity of space.

Fig. 1 illustrates the calculated relations of atomic number to N/Si ratio and resolution to atomic number. When N/Si ratio is much lower than 1.33, the films are Si-rich. With the increase of N/Si ratio, the films become stoichiometric and even have excessive amounts of N. The increased N/Si ratio leads to a decrease of atomic number and is consequently contribute to improving resolution.

3. Experiments

The experimental procedure starts with 8-in. silicon wafers. 150 nm-thick SiN_x films are deposited by a Bruce low-pressure chemical vapor deposition (LPCVD) furnace using ammonia (NH_3) and dichlorosilane (DCS) as the source materials. The deposition temperature is 780 °C, and the total deposition pressure is 300 mTorr. The NH_3/DCS gas ratio is ranged from 0.25 to 4.5 in order to obtain different SiN_x films.

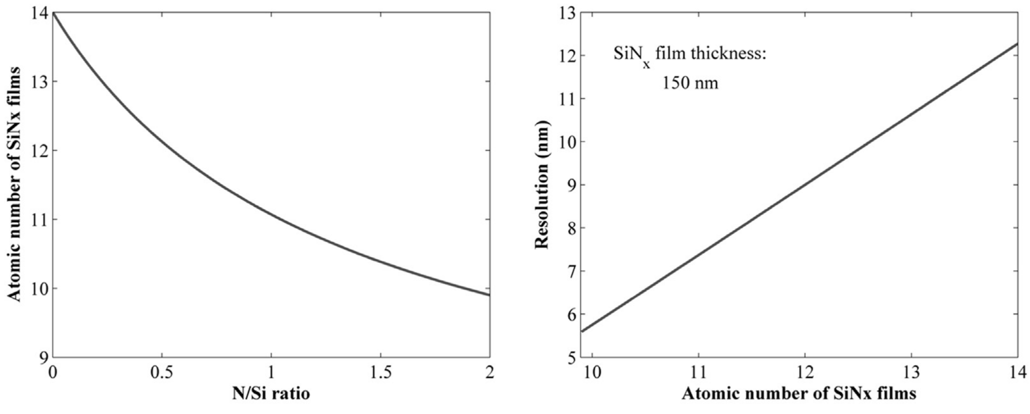
After that, the back-side SiN_x films are removed by plasma etching. The deposited low stress Si-rich SiN_x films are used as references, and the deposited SiN_x films, which have the highest N/Si ratio, are implanted with N by a M5525100-1UM implanter. N is chosen because it is an element that has relatively low atomic number in SiN_x films. The implantation doses varying from 1×10^{14} to 5×10^{15} cm^{-2} are investigated, while the implantation energy is set to be 55 keV for the reason that its corresponding project range is in the middle of the films. All the N^+-implanted SiN_x films are annealed by a furnace for 30 min in dry N_2 ambience to recover damages. The anneal temperature covers a range from 450 to 850 °C.

The stress is measured with wafer curvature measurement technique by a Kla Tencor FLX 2320S. The chemistry composition is determined by Auger electron spectroscopy (AES) using a PHI 700. The structural characterization is studied by a Thermo Scientific Nicolet 6700 Fourier transform infrared (FTIR) spectroscopy. The hardness and Young's modulus are analyzed using a nanoindentation (Agilent Nano Indenter G200) operated in continuous stiffness mode. To inspect the chemical properties, the SiN_x films are separately etched in buffered oxide etch (BOE, 25 °C, 12.5 wt%), tetramethylammonium hydroxide (TMAH, 70 °C, 2.3 wt%) and potassium hydroxide (KOH, 80 °C, 33 wt %). A film analysis metrology system (Nanospec 9100) is used to get the film thickness before and after etch, so that the etch rate is obtained.

4. Results

Fig. 2 shows the measured stress and N/Si ratio as a function of NH_3/ DCS gas ratio. The N/Si ratio in deposited SiN_x films continuously increases from 0.66 with increasing NH_3/DCS gas ratio, and is stabilized at about 1.31 when NH_3/DCS gas ratio goes beyond 2.5. In other words, the increase of NH_3/DCS gas ratio is responsible for a higher N/Si ratio. As the N/Si ratio approaches stoichiometric, further increase in NH_3/DCS gas ratio dose not change N/Si ratio appreciably. For the Si-rich SiN_x films (N/Si = 0.66), they have a low stress of 126 MPa. For the NS SiN_x films (N/Si = 1.31), there are more Si–N bonds, and as a result their stress is as large as 1143 MPa.

The NS SiN_x films are implanted with N. Fig. 3 shows the measured stress and N/Si ratio as a function of implantation dose. To demonstrate the details of implanted films, the atomic concentration profiles of Si and N along the film thickness are inserted. With increasing implantation dose, the stress decreases rapidly and reaches a minimum of 11 MPa. Meanwhile, the N/Si ratio is independent on implantation. A compressive stress is induced by the atomic collisions to offset the initial stress, and the more implantation dose is, the larger compressive



(a) (b)

Fig. 1. Theoretical relations of (a) atomic number of SiN_x films to N/Si ratio and (b) resolution to atomic number of SiN_x films.