Nuclear Instruments and Methods in Physics Research B 349 (2015) 90–95

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

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

Effect of helium ion beam treatment on the etching rate of silicon nitride

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ARTICLE INFO

Article history:
Received 23 December 2014
Received in revised form 5 February 2015
Accepted 17 February 2015
Available online 3 March 2015

Keywords:
Ion beam enhanced etching
Ion implantation
Helium ion microscope
Silicon nitride

ABSTRACT

We investigated the effect of the helium ion implantation on the etching rate of silicon nitride in hydrofluoric acid. 30 keV helium ions were implanted into a 500-nm-thick silicon nitride film on silicon. Ion fluences from 10^{15} to 10^{17} cm^{-2} were used. Etching was performed in a hydrofluoric acid solution. All samples were investigated with a scanning electron microscope and atomic force microscope. It was found that helium ion implantation can increase the etching rate by a factor of three. This results in the formation of a well in the implanted area after etching. The maximum depth of the well is about 180 nm and is limited by the penetration depth of 30 keV helium ions. Two possible reasons for enhanced etching are suggested: enhancement by ion-induced defects and electrostatic interaction of ions of the etchant with ion-induced space charge of silicon nitride. The recombination of ion-induced defects is also discussed.

1. Introduction

Ion beam treatment techniques, including ion implantation (II), are commonly used modern technologies in microelectronics and nanotechnology. One of the possible applications of II is ion induced defect engineering [1]. Ion beam induced defects can change electrical, optical and chemical properties of materials. One of such properties is the etching rate. It is known that ion implantation change the etching rate of different materials, such as sapphire [2,3], silicon oxide [4], lithium niobate [5,6] and silicon [7]. This effect is referred to as ion beam enhanced etching (IBEE) [6] and can be used for the production of structures with predefined geometry by means of local ion implantation. There are two ways to perform local II: implantation through the mask [8,9] or local implantation by means of focused ion beam (FIB) [4,7,10,11]. The latter method provides an opportunity to produce any geometry of implanted area by means of point-by-point scanning, whereas the capabilities of the former are limited by the geometry of the mask. The dose of local implantation with FIB can be varied by means of variation of the dwell time in each point, and the dose of implantation through the mask is constant over the entire area of implantation.

A focused ion beam was previously used for modification of etching characteristics of silicon oxide [4,10] and silicon [7,11]. Most of conventional FIB systems use gallium liquid metal ion source (LMIS) or Au–Si eutectic LMIS. In this case, implantation of target material with gallium [7,10,11] or silicon [4] takes place. These dopants may change electronic properties of material, and this change is undesirable for many applications. The implantation of ions of inert gases is a possible alternative.

Helium ion microscope (HIM) is a new type of FIB with gas field ion source. HIM was developed few years ago [12–14]. Spatial resolution of surface sputtering in HIM is higher than sputtering resolution of conventional gallium FIB [15–17]. This fact in combination with implantation of inert gas makes helium ion microscope promising tool for local II. Application of this method requires better understanding of the mechanisms of IBEE with helium ions. Effect of He ion implantation on etching characteristics of aluminum oxide [9,18] and lithium niobate [6,8] was previously demonstrated. In this work we investigate the effect of the helium ion beam treatment on the etching rate of silicon nitride.

Silicon nitride is one of the traditional materials of microelectronic industry. There are several new applications of silicon nitride in modern nanotechnology such as inorganic resist [19], material for nanoimprint lithography molds [20,21], and thin membrane for the detection of molecules [22]. In this paper we describe the enhancement of the etching rate of helium implanted silicon nitride and discuss the origin of this effect.

2. Experiment

In our work we investigated samples of silicon nitride on silicon (Si_3N_4–Si). 500-nm-thick silicon nitride film was grown by low-

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http://dx.doi.org/10.1016/j.nimb.2015.02.054
0168-583X/

pressure chemical vapor deposition (LPCVD) from silane and ammonia.

Helium ion microscope Zeiss Orion equipped with NanoMaker lithography system was used for helium ion beam treatment. Samples were locally exposed to helium ions with energy of 30 keV and beam current of 10 pA. The spot size of helium beam was of about 1 nm. Round areas with the diameter of 2 micrometers were exposed by point-by-point scanning. The distance between points was 2 nm, and dwell time was varied to obtain ion fluence ranging from 10^{15} to 10^{17} cm^{-2}. Ion implantation was performed at room temperature (293 K). After II samples were etched with 30% hydrofluoric acid water solution. Time of etching was varied from 1 to 300 s. Etching was performed at room temperature (293 K). Immediately after etching samples were rinsed with deionized water and dried with the stream of compressed air.

All samples were investigated with atomic force microscope (AFM) NT-MDT NTEGRA PRIMA and with a scanning electron microscope (SEM) Zeiss Merlin.

3. Results

All samples were investigated with SEM and AFM. No changes of a surface of as-implanted samples were observed before etching. After etching the formation of round wells was observed. Each well corresponded to the exposed area. The depth of each well was measured with AFM. SEM images of these wells and AFM profiles are depicted in Fig. 1. One can easily see from Fig. 1 that the depth of the well increases when the time of etching increases. The dependence of the depth of the well on ion fluence is depicted in Fig. 2. At short etching times mesa type prominence is observed if fluence is over 6 * 10^{16} cm^{-2}. The height of this mesa was measured and depicted in Fig. 2 as a negative depth. We can see from Fig. 2 that the depth of the well increases when time of etching increases from 1 to 50 s. In this case the maximum of the depth of the well corresponds to ion fluence of about 8×10^{15} cm^{-2}. If time of etching is over 100 s, the depth of the well reaches saturation for ion fluence over 5×10^{15} cm^{-2}. Maximum depth is obtained if time of etching is 100 s. After 200 s of etching the depth of the well slightly decreases and does not change for etching time of 300 s. It should be noted that the walls of the well are sloping if etching time is 200 s (Fig. 1c) whereas no slope is observed in the case of 50 s of etching (Fig. 1b).

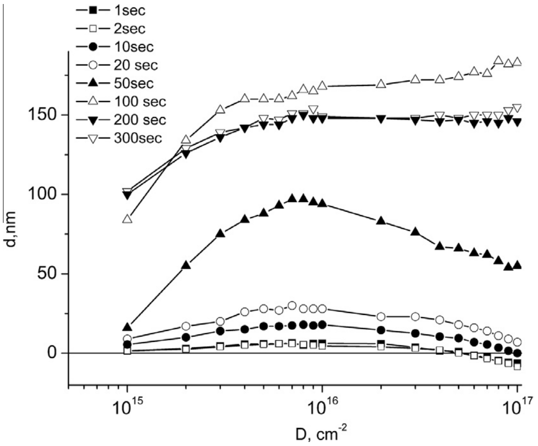

Fig. 2. The dependence of the depth of the well on the ion fluence.

The thickness of initial (unexposed) silicon nitride film of etched samples was measured from SEM images of sample cross-section. The etching rate of initial silicon nitride was found to be constant over the film thickness.

4. Discussion

Formation of wells means that the etching rate of helium implanted area increases as a result of II. Process of etching of silicon nitride includes the formation of silicon fluorides and subsequent dissolution of silicon fluorides in water. Linking of fluorine to silicon requires opening of silicon–nitrogen bond. The presence of the dangling bonds in silicon nitride assists the linking of fluorine to silicon and accelerates the etching process. Thus increase of the etching rate can be explained by the generation of ion-induced defects. We calculate the dependence of the etching rate on the depth and compare it with the concentration of defects obtained from Monte-Carlo simulation.

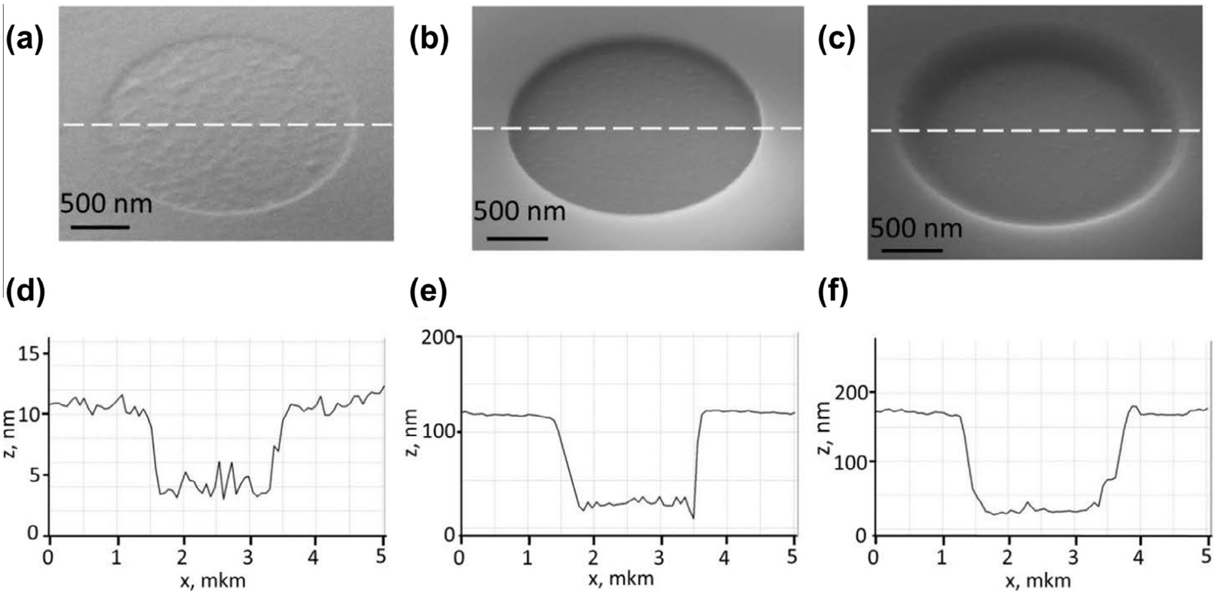

Fig. 1. SEM images (a)–(c) and AFM-profiles (d)–(f) of wells formed after etching. Sample tilt in SEM images is 45°. AFM-profiles are measured along the bright dashed line in SEM images. Ion fluence is 10^{16} cm^{-2}. Time of etching: (a) and (d) – 1 s, (b) and (e) – 50 s, (c) and (f) – 200 s.