Applied Surface Science 273 (2013) 107–110

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Metal-assisted homogeneous etching of single crystal silicon: A novel approach to obtain an ultra-thin silicon wafer

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ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form 20 January 2013
Accepted 28 January 2013
Available online 4 February 2013

Keywords:
Thin silicon wafer
Homogeneous etching
Holes
MACE

ABSTRACT

Homogeneous etching of silicon is achieved through one-step metal-assisted chemical etching (MACE), which offers a simple route to obtain the ultra-thin silicon wafer with thickness below 50 μm. The surface of the ultra-thin silicon wafer obtained by this method is smooth at the nanometer scale, and its surface roughness is around 10 nm. The homogenous etching mechanism is discussed in terms of the hole injection principle. It's found that the introduction of a high concentration of H_2O_2 facilitates the uniform distribution of the holes injected on the silicon surface, causing the homogeneous etching of the silicon. Meanwhile, the thinning is uniform across a large wafer area, and ultra thin silicon wafers up to 4 in. in diameter were obtained. Furthermore, any thickness of silicon wafer within 30–180 μm can be obtained by modulating the etching process accurately.

1. Introduction

The metal-assisted chemical etching (MACE) method has emerged as a simple method to fashion materials at nanometer length scales [1–3]. The common MACE process has a preferential etching orientation, such as, the preferential etching direction is along ⟨1 0 0⟩ orientation for single crystal silicon substrate covered with noble metal nanoparticles [4]. Just because of the selective etching, MACE can be used to prepare porous silicon [5,6], and nanowire array [7,8]. However, if the homogeneous etching can be achieved on the silicon substrate, the MACE method will get new fields of applications. First of all, this homogeneous etching technique can be used to perform the thinning of silicon wafer. At present, the thin silicon wafer with a thickness under 50 μm is a promising building block for a range of microelectronics and microsystems, such as 3D integrated circuits [9], ultra-thin chips [10], thin silicon solar cell [11] and flexible electronics [12].

The work described herein uses the simple one-step MACE method to realize the homogeneous etching of silicon. The ultra-thin silicon with a thickness of 30 μm is obtained, while the surface roughness is around 10 nm. Meanwhile, the mechanise that explains the homogenous etching is proposed. Furthermore, any thickness of silicon wafer within 30–180 μm can be obtained by modulating the etching process (etching rate, reaction time, and et al.). The facile, practical method to achieve ultra thin silicon should be of particular interest, due to its low cost, and absence of a residual mechanically damaged layer after general etching.

2. Experimental

P-type monocrystalline silicon (1 0 0) samples with a thickness of 525 μm were used as the starting samples. Generally, we used small silicon sample with the size of 1.5 cm × 1.5 cm, for the large scale investigation, we used 4 in. Si wafer directly. The Si samples were cleaned using acetone, absolute ethyl alcohol and deionized water in the ultrasonic condition, respectively. The cleaned Si samples were dipped into dilute HF solution to remove native oxide. Following the pretreated step, the Si samples were immediately placed into the etching solution for an appropriate duration. Here, the etching solution contained HF, $AgNO_3$, and H_2O_2 with suitable ratio. The reaction temperature was in the range of 10–50 °C.

Surface morphology and transverse thickness of the etched Si samples were characterized by scanning electron microscope (SEM) with FEI Quanta 200F. Surface roughness of the etched Si samples was measured by atomic force microscope (AFM) with Veeco Dimension 3100V. Ag information in thin silicon wafer was detected by X-ray fluorescence spectroscopy with Thermo Fisher K-Alpha.

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http://dx.doi.org/10.1016/j.apsusc.2013.01.196

3. Results and discussion

Using one-step MACE method, which combines the metal catalyst deposition with the silicon dissolution in the mixture solution at the same time, we got the homogeneous etching of the silicon, as shown in the Fig. 1. The surface morphology of the etched silicon is shown in Fig. 1a using 3D AFM image. The corresponding average roughness is around 13 nm, which is smooth at the nanometer scale, rather than smooth at macroscopic level [13]. To vividly illustrate the surface smoothness of the etched silicon, the reflectance comparison of the silicon wafers before and after etching is shown in Fig. 1b. Their reflectance values have very little variation in the wavelength range of 300–1000 nm, suggesting that the surface of the etched silicon is as smooth as the original wafer, which is absolutely different with the nanopore structure obtained by silver-catalyzed etching of silicon in HF/H_2O_2 solution [5]. The surface roughness of the etched silicon wafer is varying as a function of etch conditions; there is still a large space to improve by further optimizing the process parameters.

In addition, the ultra-thin silicon sample with a thickness below 50 μm can be achieved simply. In Fig. 1d, it can be seen that the average thickness of the silicon wafer decreased from 525 μm to 30 μm after 22 min etching reaction. And this method is suitable for large scale thinning application. A 4 in. silicon wafer with a thickness of 98 μm, obtained by this method, is ready for large-scale use, as depicted in Fig. 1c.

What's the mechanism that explains the observation of the homogeneous etching of silicon with MACE method? In MACE process, as catalyst agents, noble metal nanoparticles catalyze the production of holes from chemical oxidants, commonly H_2O_2, which are then injected into the valence band of the silicon, resulting in the anisotropic dissolution of the silicon [1,14,15]. Therefore, the diffusion of the injected holes around the silicon underneath the noble metal particles is the key factor to the dissolution of the silicon. To enable homogeneous etching of silicon in the MACE process, a homogeneous distribution of the injected holes on the silicon surface is essential. To achieve this goal, in the present work, both excessive H_2O_2 and a suitable concentration $AgNO_3$ are introduced into HF solution, which facilitate the generation and the diffusion of holes, and densify the silver nanoparticles, finally leading to the homogeneous etching of the silicon.

In details, the basic processes of the silicon selective etching by MACE mainly includes the oxidation of silicon by injected holes and the dissolution in the HF solutions by reaction (1). At the silicon areas with metal covered, the hole injection from metal into the silicon can perform with the presence of oxidizing agents by reaction (2). However, at the silicon areas without metal covered, the direct injection of hole from solution is impossible. Therefore, usually the distribution of holes on the surface is un-uniform, causing selective etching of silicon. However, at the silicon areas without metal covered, the slightly etching layer (several nanometers in thickness) was observed [1,16–18]. And the etching layer became obvious with increasing the content of oxidizing agents in the etchant, which is related to the diffusion of the injected holes around the silicon underneath the metal [1]. Hence, to get the homogeneous etching of silicon, a uniform distribution of holes on the silicon surface is crucial, requiring fast diffusion of injected holes to the silicon surface there without metal covered. In view of this point, a dense distribution of Ag particles, and Ag nanoparticles with small size are able to meet this requirement. These small and dense Ag nanoparticles can provide much more sites of hole injection and also shorten the diffusion distance of the injected holes in the vicinage of Ag NPs, which facilitate the homogeneous distribution of holes on the silicon surface.

$$Si + 6HF + 4h^+ \rightarrow H_2SiF_6 + 4H^+ \quad (1)$$

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+ \quad (2)$$

To make sure these analyses, the etchings of silicon wafers as a function of H_2O_2 concentration were investigated. Fig. 2 shows SEM images of the etched silicon samples in the presence of H_2O_2 with different concentrations. When the concentration of H_2O_2 is low, as can be seen from Fig. 1a, the surface of resultant silicon is textured by silicon nanowires arrays. With the increasing of H_2O_2 concentration, the unordered silicon pillars form on the silicon substrate (as shown in Fig. 2b). It is noted that the porous layer is observed on the surface of these pillars (as displayed in Fig. 2b inset). When the concentration of H_2O_2 increases to 1 M in the etching bath, the silicon surface appears quite flat, as shown in Fig. 2c. These results indicate that the etching of the single crystal silicon can vary from selective etching to homogeneous etching with the increase of H_2O_2 concentration. In theory, the addition of massive H_2O_2 into HF/$AgNO_3$

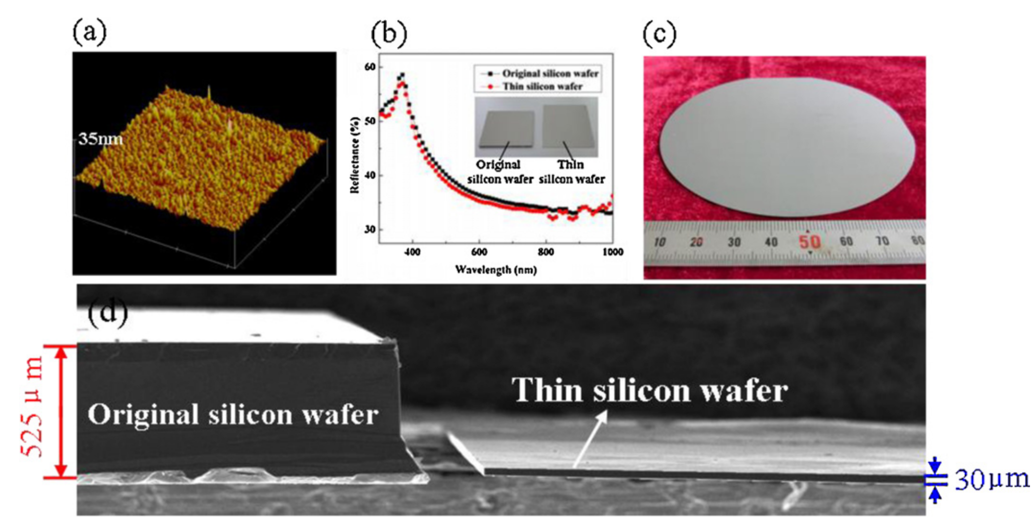

Fig. 1. (a) 3D AFM image of the silicon surface etched for 25 min at 30 °C; (b) The reflectance comparison of the silicon wafer before and after etching; (c) A picture of 4 in. silicon wafer thinned in the solution for 20 min at 50 °C; (d) The comparison of the original silicon wafer and the thin silicon wafer, which obtained through homogeneously etching the silicon sample for 22 min at 30 °C; The inset in Fig. 1b is the photos of the original silicon wafer and the thin silicon wafer. All etchant solution has same composite and concentration, containing 4.6 M HF, 0.02 M $AgNO_3$, and 5 M H_2O_2.