Applied Surface Science 371 (2016) 129–138

Contents lists available at ScienceDirect

Applied Surface Science

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

Metal-assisted chemical etching of Ge surface and its effect on photovoltaic devices

Seunghyo Lee, Hyeokseong Choo, Changheon Kim, Eunseok Oh, Dongwan Seo, Sangwoo Lim*

Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, South Korea

ARTICLE INFO

Article history:
Received 26 June 2015
Received in revised form 7 February 2016
Accepted 22 February 2016
Available online 2 March 2016

Keywords:
Ge
Metal-assisted chemical etching
Orientation
Anisotropic etching
Solar cell

ABSTRACT

Ge surfaces were etched by means of metal-assisted chemical etching (MaCE). The behavior of the MaCE reaction in diluted H_2O_2 was compared with that of a conventional etchant of $HF/H_2O_2/H_2O$ mixture (FPM). Herein we first report that a pyramidal structure on Ge (0 0 1) can be prepared by MaCE in dilute H_2O_2 solution, without the use of HF. Contrastingly, an octagonal trench structure was prepared by 4/5/1 FPM treatment of Ge (0 0 1) surface. This octagonal structure consisted of a square base, four large facets connected to the base, and other four small facets adjacent to the four large facets, which were considered to be (0 0 1), {1 1 0}, and {1 1 1}, respectively. The octagonal trench was formed as a result of the difference in etch rate of Ge depending on the orientation: {1 0 0} > {1 1 0} > {1 1 1}. Ge surfaces treated by MaCE exhibited improved solar cell efficiency due to their improved light absorption, which led to significant increases in the cells' short circuit current and fill factor. The results suggest that optimized MaCE procedures can be an effective method to improve the performance of Ge-based photovoltaic devices.

1. Introduction

MaCE was initially introduced as a means to prepare high-aspect-ratio Si nanostructures. MaCE has attracted great attention in recent years for several reasons [1]. MaCE can produce nanostructures having high aspect ratios and surface-to-volume ratios [2,3], because the electrochemical etching of Si, which is of diamond cubic crystal structure, is anisotropic and proceeds selectively along the <100> orientation [4,5], In addition, it is a simple and low-cost method. Therefore, MaCE has been applied to the fabrication of devices for various applications such as solar energy conversion, energy storage, chemical and biological sensing, and thermal energy conversion [6–9].

While extensive efforts involving MaCE have focused on Si, MaCE has also been used for the fabrication of GaAs nanowires [10], GaAs hole arrays [11] and GaN nanowires [12]. However, there has been a limited number of reports on MaCE of germanium [13–15], a carbon-group element that is chemically similar to silicon. Because Ge has a higher carrier mobility than Si at a given electric field, the nanostructures of Ge could be easily prepared by means of MaCE, which would enhance the fabrication of various types of Ge-based electronic and optical devices. However, MaCE of Ge is difficult due to the oxidation and dissolution of Ge, even on regions without metal particles [16]. During the MaCE process, the metal particles act as local cathodes, which reduces the solution by catalytic reactions, and the anode reaction takes place on the semiconductor surface that is in contact with the metal, thereby oxidizing and dissolving the semiconductor substrate [1,17–19]. Because the electrons move from the anode to the cathode, the etching proceeds quickest in regions covered by metal particles. However, Ge is oxidized not only under the catalytic metal particles, but also on the Ge surface directly exposed to the etchant solution. Therefore, all the Ge surface, both with and without coverage by metal particles, can be dissolved in the liquid solution. Although Ge etching rates differ between regions covered and not covered by the catalytic metal, it may be not easy to achieve Ge nanostructures with aspect ratios as high as those obtainable on Si. Actually, a report of Kawase et al. gives an idea of Ge MaCE [13]; they demonstrated MaCE of Ge (1 0 0) in oxygen dissolved water, producing pyramidal etch pits with (1 1 1) facets. In addition, the application of MaCE to nanoscale patterning via metal-coated cantilevers was introduced. However, the detailed effects of solution composition and Ge surface orientation on Ge MaCE have not been thoroughly investigated in previous literature.

* Corresponding author.
E-mail address: swlim@yonsei.ac.kr (S. Lim).

http://dx.doi.org/10.1016/j.apsusc.2016.02.197

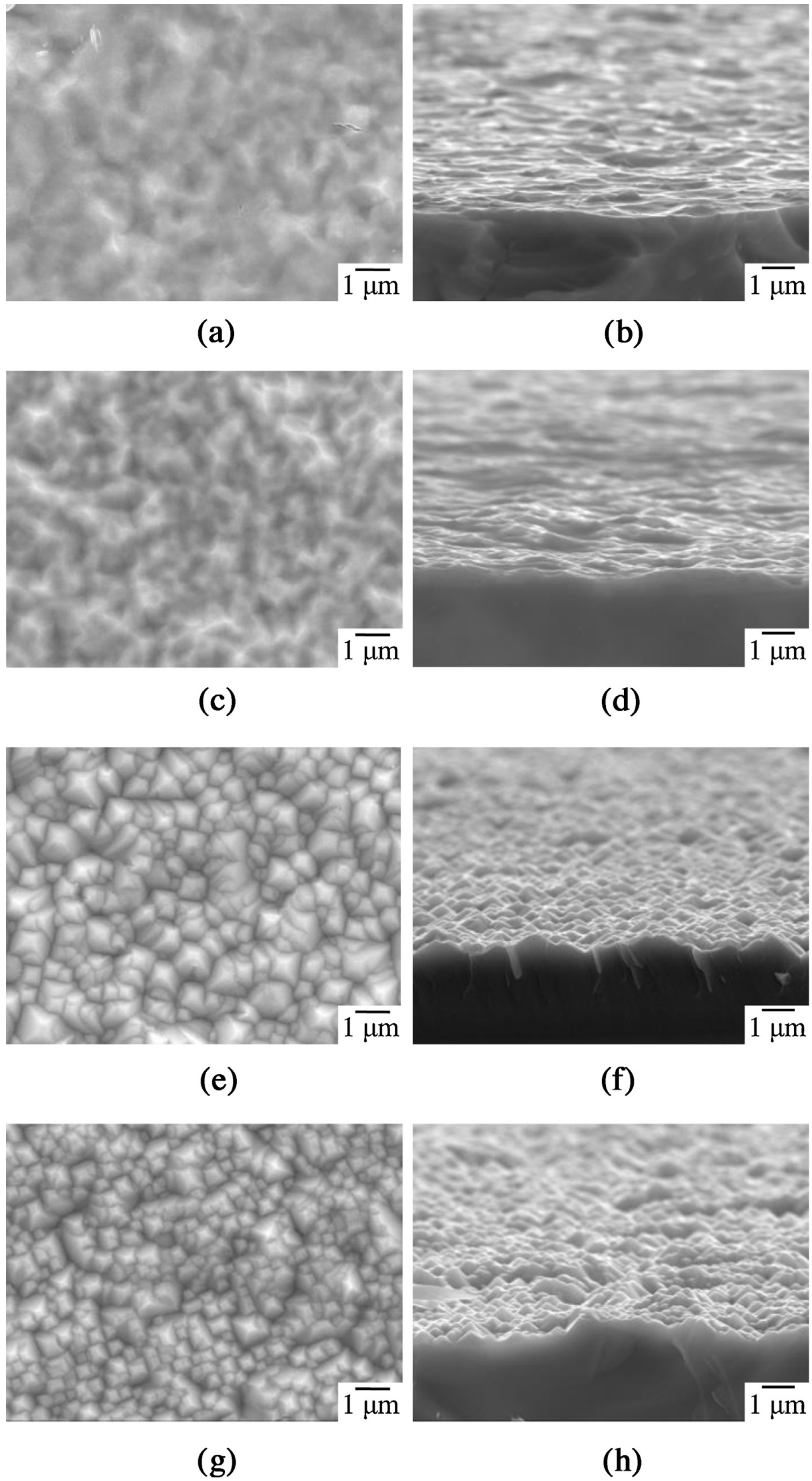

Fig. 1. SEM surface images of Ge (1 0 0) wafers that underwent MaCE for 30 min in 30% H_2O_2/H_2O mixtures of various dilution ratios: (a) and (b) 1/4, (c) and (d) 1/19, (e) and (f) 1/99, and (g) and (h) 1/399.