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Optimization of silver-assisted nano-pillar etching process in silicon

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ABSTRACT

In this study, a respond surface methodology (RSM) model is developed using three-level Box–Behnken experimental design (BBD) technique. This model is developed to investigate the influence of metal-assisted chemical etching (MACE) process variables on the nanopillars profiles created in single crystalline silicon (Si) substrate. Design-Expert® software (version 7.1) is employed in formulating the RSM model based on five critical process variables: (*A*) concentration of silver (Ag), (*B*) concentration of hydrofluoric acid (HF), (*C*) concentration of hydrogen peroxide (H_2O_2), (*D*) deposition time, and (*E*) etching time. This model is supported by data from 46 experimental configurations. Etched profiles as a function of lateral etching rate, vertical etching rate, height, size and separation between the Si trenches and etching uniformity are characterized using field emission scanning electron microscope (FE-SEM). A quadratic regression model is developed to correlate critical process variables and is validated using the analysis of variance (ANOVA) methodology. The model exhibits near-linear dependence of lateral and vertical etching rates on both the H_2O_2 concentration and etching time. The predicted model is in good agreement with the experimental data where R^2 is equal to 0.80 and 0.67 for the etching rate and lateral etching respectively. The optimized result shows minimum lateral etching with the average pore size of about 69 nm while the maximum etching rate is estimated at around 360 nm/min. The model demonstrates that the etching process uniformity is not influenced by either the etchant concentration or the etching time. This lack of uniformity could be attributed to the surface condition of the wafer. Optimization of the process parameters show adequate accuracy of the model with acceptable percentage errors of 6%, 59%, 1.8%, 38% and 61% for determination of the height, separation, size, the pore size and the etching rate respectively.

1. Introduction

Silicon (Si) is perhaps the most widely studied element in the periodic table. Well known for its stability at high temperature and non-toxic nature, this material has become the backbone of the integrated-electronics industry for decades. Extensive studies have been conducted on various aspects of Si technology including its growth, micro and nano scale etching, and doping. Synthesis of nano-scale structures in Si has attracted tremendous attention over the past few years. This is due to their wide range of applicability in numerous fields including optoelectronics, micro, and nano-electronics [1,2], biological and chemical sensors [3], and energy conversion and storage [4]. Lithographically defined, reactive-ion etched nanostructures have also found extensive applications as templates for pseudomorphic heteroepitaxial growth of Ge and GaAs on Si [5–7]. The role of nanostructures is to getter defects at the interface layer. While leading to high-quality epitaxial growth on Si, the lithography approach to nano-patterning is diffraction-limited and expensive. An inexpensive, non-lithography based process capable of patterning large area is desirable for epitaxial growth applications.

Fabrication of the deeply etched anisotropic high aspect ratio columnar Si nanostructures is often a complex and expensive process. Two-dimensional Si nanostructures are either fabricated with a top-down or bottom-up approach. In a top-down approach, a predefined template is used as an etch mask to form deeply etched anisotropic features [5], while for a bottom-up approach, a template based growth process is used to form whisker-like high aspect ratio columnar nanostructures [8]. Synthesis mechanisms for both

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approaches can be selected from an extensive portfolio of methods and processes based on application requirements. The most common methods include catalysis-assisted vapor-liquid-solid (VLS) growth technique [9,10], metal-catalyzed molecular beam epitaxy (MBE) [11,12], reactive ion etching (RIE) [13] and chemical vapor deposition (CVD) [14]. Unfortunately, the cost of using these methods is high, often requiring expensive semiconductor processing tools, high process temperatures, and toxic gasses.

In the recent years, the synthesis of Si nanostructures, based on metal-assisted rapid oxidation of Si and its subsequent chemical etching (MACE) technique, has attracted significant attention due to its inherent simplicity and ability to generate high aspect ratio columnar Si nanostructures [15–17]. MACE in Si can be carried out by using either the one-step or two-step process. The one-step MACE was first introduced by Peng et al., where etching of Si substrates was conducted in aqueous solution of $AgNO_3$:HF at low temperatures [18]. This method is also referred to as electroless metal deposition technique. In this method, aligned high aspect ratio nano-scale Si columnar profiles arrayed perpendicular to the Si surface was observed largely attributed to selective etching [16,18,19].

In two-step MACE, deposition of metal catalyst and etching of Si substrates happen in two separate processes. The first step involves deposition of the metal catalyst onto the Si substrates followed by etching in oxide containing solution. The metal catalysts are either spin coated [20], evaporated [21–23], sputtered [24] or deposited using electroless metal deposition technique [25,26] on the surface of the Si substrates. The latter method is of current interest of this study as this method is simple and inexpensive, yet able to produce the desired high aspect ratio nanostructures.

The two-step MACE synthesis of Si nanostructures is influenced by several process factors including etchant concentration and composition, deposition time and temperature as well as etching time and temperature [27–29]. Published work suggests that etching in oxide containing solution in this case H_2O_2, results in formation of nano-pores on the sidewalls of the Si nanostructures due to lateral etching [27]. High concentration of H_2O_2 promotes dissolution of Ag nanoparticles that result in reduction of it size and increase in the concentration of Ag^+ ions. These Ag^+ ions are diffused out forming smaller Ag nanoparticle deposited on the sidewalls of the Si structures and etch perpendicular to the surface of the Si structures forming cone-shaped micro-pores with rough surface [30].

According to Smith et al., the trail of pores are fanned out at the angle of about 68° which suggest a linear relationship where the ratio is estimated at 2.5:1 (nanostructure length: porous Si thickness) [15]. This explains the formation of cone shape structures formed when etching is conducted at very high concentration of H_2O_2. Reduced concentration of H_2O_2 retarded the acute reaction of dissolution and nucleation of Ag nanoparticle. At low H_2O_2 concentration, the Ag+ ions are confined around the vicinity of the Ag nanoparticles forming thin layer of nano-pores on the sidewalls of the Si nanostructures [30].

Despite the extensive literature on various aspects of MACE process, relatively little work has been reported on systematic analysis of process parameters on etched Si profiles. Yuangyai and Nembhard, in their book suggest that the Design of Experiment (DoE) is a practical solution for optimization of nanotechnology and nanomanufacturing as it minimizes the number of laboratory works to be done [31]. There are several methods to choose from depending on the affecting variables, number of levels and design variations. The process variable, otherwise known as the 'factor', can be either quantitative or qualitative. For each selected factor, the variable values in the range of interest are referred to as levels [32]. When there is only one factor to be considered, a single comparison method is used to determine the significance of that factor. In the case of a process based on multiple factors, the number of levels for each factor determines the most suitable method applied. Among all, the most common methods are the complete randomized design (CRD), two-level factorial design, response surface methodology (RSM) [33,34] and Taguchi's method [35].

A recent study was conducted by Ali and Masoud on the used of Taguchi method to investigate the effect of various factors on the formation of Si nanostructures produced by using the MACE technique. In this study, four process parameters that include noble metal, etching time and temperature as well as H_2O_2 concentration were statistically evaluated to determine the influence of each process parameters in the formation of Si nanostructures. However, despite the systematic evaluation of various process parameters involves in MACE of Si, optimizations of each process parameters were not conducted [36].

In the RSM method, the principle objective is the optimization of process variables with mathematical and statistical techniques. The RSM method, originally developed by Box and Wilson, is widely practiced in chemical and processing industries for designing experiments, evaluating variables and the optimization of process parameters [32]. The techniques used in RSM method include central composite design (CCD) [37], Doehlert designs [38], and Box–Behnken design (BBD) [39,40]. Because of its simplicity, CCD is commonly used in analytical procedures. However, BBD technique is reckoned superior especially when it is applied for quadratic RSM with three or more factors [41]. Ferreira et al., have reported that the BBD is more efficient in comparison with the CCD while requiring fewer number of runs [42].

Study by Chen et al. showed that the RSM method was able to provide a better insight on the effects of process parameters involved in the formation of Si structures using deep reactive ion etching technique. In addition, the RSM model provided a more systematic approach for process optimization. From the statistical analysis, correlations between surface morphology and operating conditions as well as between fracture strength and surface roughness were observed [43]. In another study by Ting et al., comparison between the use of RSM method and Artificial Neural Network (ANN) were conducted. In this study, CCD design was chosen with three numeric factors, one categorical factors and five central point generating 40 runs in total. It was found that the model prediction using RSM method was able to provide up to 95% confident level. The results were comparable with the model prediction using ANN method [44].

Statistical analysis of MACE reported here is aimed at the optimization of the etching process for the synthesis of uniform, repeatable, nano-pillar profiles in crystalline Si substrates. As part of the synthesis process development, RSM model based on three-level BBD technique is developed. Design-Expert® software (version 7.1) is used in formulating a model based on five factors: concentrations of Ag, HF, H_2O_2, deposition time, and etching time [45]. A wide range of Si nano-pillars profiles are created in (100) Si substrate and are characterized with Hitachi S8000 ultra-high resolution field emission scanning electron microscopy (FESEM).

2. Model development with statistical analysis

The RSM model, based on Design-Expert® software (version 7.1), is developed by using three-level BBD experimental design technique. Fig. 1 describes the BBD design, in terms of a rotatable or nearly rotatable three-level factorial design without any points at the vertices [46]. Each factor is assessed at three levels: minimum (low), central (medium), and maximum (high). The number of experiments (N) required for the development of the BBD is given by

$$N = 2k(k-1) + C_o \quad (1)$$