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Fabrication of antireflective layers on silicon using metal-assisted chemical etching with in situ deposition of silver nanoparticle catalysts

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ABSTRACT

Ag particle-assisted chemical etching of silicon wafers in HF/H_2O_2 is of interest for its potential to produce antireflective layers for solar cells. In this work, Ag films containing both nanoscale ($d < 100$ nm) and microscale ($d < 1$ μm) particles were deposited through the silver-mirror reaction on planar *p*-Si(111), planar *p*-Si(100) and *p*-Si(100) pre-etched in KOH/isopropanol to produce pyramidal textures. Subsequently, these wafers were subjected to metal-assisted chemical etching (MacEtch) in 1:1:1 (v:v:v) HF(49%):H_2O_2(30%):EtOH solutions, to produce porous silicon (PSi) containing both micro- and nanoscale roughness features. The resulting surfaces exhibit morphologies that evolve with processing conditions, especially the absence/presence of pyramidal textures and the time the structure is subjected to MacEtch. Under optimal conditions excellent anti-reflection behavior is observed with surface reflectivities being reduced below 10% for either *p*-Si(100) or *p*-Si(111) surfaces. For *p*-Si(100) better results ($R \sim 5\%$) were obtained for 30 min KOH/isopropanol pre-etch than for either no pre-etch or longer (60 min) pre-etch. The influence of the reductant on Ag particle deposition on *p*-Si(111) was studied, and MacEtch catalyzed by Ag produced from acetaldehyde reductant produced surfaces with lower reflectivities than those with glucose reductant.

1. Introduction

Fabrication of antireflective layers on all kinds of silicon surfaces has attracted attention since the 1980s as a key technology to effectively improve the efficiency of silicon solar cells, both in first-generation photovoltaic cells based on bulk materials and second-generation structures based on thin-films [1–15]. Simple, practical methods to texturize silicon surfaces for anti-reflection applications that utilize wet chemical etching are of particular interest, due to their low cost, compatibility with mass production and absence of a residual mechanically damaged layer after etching.

Wet etching approaches can be categorized grossly into alkaline and acidic etches. Alkaline etches are valued for their ability to produce randomly distributed inverted [2,4,14] or upright pyramids [1,3,15] on monocrystalline Si(100) surfaces, based on the fact that different crystallographic planes exhibit different etching rates. These structures can reduce the surface reflectivity drastically in the 400–1200 nm spectral region [3,15], the wavelength band in which most of the energy of the solar spectrum is contained at normal incidence. However, the average reflectivity of these materials remains above 10%, the process must be carried out at elevated temperatures, and sometimes masks are also needed to spatially direct the etching [14]. Acidic etching, typically carried out in $HF/HNO_3/CH_3COOH$ or $HF/HNO_3/H_2O$, is more effective for polycrystalline, rather than monocrystalline, silicon, because it is isotropic [9]. However, the reactions can be difficult to control and can be accompanied by the evolution of undesirable gases, like NO [16,17].

To address some of these processing issues, a novel acid-based oxidation process, termed metal-assisted chemical etching (MacEtch) has been introduced [6,7,10,12,18–21]. MacEtch can be applied to both elemental and compound semiconductors, but it was used initially to prepare porous Si (PSi) from *p*-Si(100) wafers. In MacEtch, noble metal nanoparticles, typically Ag, catalyze the production of holes from chemical oxidants, commonly H_2O_2, which are then injected into the valence band of the semiconductor, resulting in the dissolution of silicon and the formation of etched structures near the particles [19,22]. Many kinds of

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functional nanostructures from 1D to 3D have been fabricated by application of the MacEtch process to silicon using Ag particle catalysts [23,24], with the final etched morphologies being directly related to the characteristics of Ag particles, *e.g.* size, initial spatial distribution, shape etc. For example, quasi-ordered rectangular and hexagonal structures are obtained by Ag-catalyzed MacEtch of *p*-Si(100) and *p*-Si(111), respectively [25]. The initial particle morphology is usually determined by the deposition conditions. Meanwhile, noble metal deposition on silicon has been extensively investigated for applications such as plasmonic coupling of incident radiation into waveguide modes of thin semiconductor photodetectors [26], enhancing layers for surface-enhanced Raman scattering (SERS) [27,28], working electrodes for Faradaic electrochemistry [12] and localizing surface plasmons to enhance the absorbance of silicon solar cells [29]. Thus, the development of Ag particle catalyzed MacEtch to produce practical antireflective layers is of considerable interest.

Here we report a new approach to the production of antireflective materials from crystalline silicon based on the reductive deposition of Ag nanoparticles from solution using the silver-mirror reaction (Tollen's reagent) [30]. Interestingly, after direct deposition of Ag particles on Si surfaces followed by MacEtch, *p*-Si(100) and (111) surfaces are obtained with surface reflectance reduced below 10%. The MacEtch process can also be applied as a second processing step to Si(100) surfaces previously texturized in KOH/IPA, and these structures are compared to those obtained from MacEtch of pristine silicon directly.

2. Experimental section

2.1. Materials

Boron-doped *p*-Si(100) and *p*-Si(111) single crystal wafers with resistivities of $\rho \sim 7$–$13\ \Omega$ cm and 8–13 Ω cm, respectively, were purchased from Emei Semiconductor Factory, China. Single-polished wafers were cut into $2.0 \times 2.0\ cm^2$ pieces. Deionized (DI) water ($\rho \sim 18.2\ M\Omega$ cm) from a Milli-Q Gradient water purification system (Millipore) was used to prepare all aqueous solutions and for rinsing. All chemicals were used directly as-received, without further purification. Hydrofluoric acid (49% electronic grade) was purchased from Transene Co. Ammonium hydroxide ($NH_3 \cdot H_2O$, 28–30% NH_3, ACS reagent) and sodium hypochlorite solution (NaOCl, 10–15%, reagent grade) were purchased from Sigma-Aldrich Co. Acetaldehyde (CH_3CHO, certified) and hydrogen peroxide (H_2O_2, 30%, certified ACS) were purchased from Fisher Scientific. Silver nitrate ($AgNO_3$, AR), glucose ($CH_2OH(CHOH)_4CHO$, AR), sodium hydroxide (NaOH, AR), potassium hydroxide (KOH, AR), nitric acid (HNO_3, 32–34%, AR), acetone (CH_3COCH_3, AR.CP), isopropyl alcohol (IPA, $(CH_3)_2CHOH$, AR) and ethanol (EtOH) (C_2H_5OH, AR) were purchased from Tianjin Chemical Reagent No. 1 Plant.

2.2. Silver particle deposition

A block diagram describing the processing flow is shown in Fig. S1 in Electronic Supplemental Information (ESI). Before experiments, the glass beakers were cleaned by boiling 10% NaOH solution for 10 min, followed by rinsing with DI water for 5 min (2 times). Ammonium hydroxide was diluted to ~2%, and acetaldehyde was diluted to ~10% using DI water. All singly-polished *p*-Si(100) and Si(111) wafers were pretreated in ~12% aqueous NaOCl for 15 min to remove surface contaminants [8]. Selected *p*-Si(100) wafers were texturized in KOH (1%)/IPA (6v%) at 80 °C for 30 or 60 min. A combination of micro- and nano-sized Ag particles was deposited on the cleaned surfaces of *p*-Si(100) and Si(111) wafers through the silver-mirror reaction after first

Table 1
MacEtch time for *p*-Si wafers.

Samples	S1[a]	S2	S3	S4	S5	S6	S7	S8[b]	S9	S10	S11	S12[b]	S13	S14	S15
***p*-Si(100)**															
Etch *t* (min)	0	10	20	30	60	120	180	0	10	20	30	0	1	5	120
Texturizing conditions	NaOCl							KOH/IPA	KOH/IPA	KOH/IPA	KOH/IPA	KOH/IPA	KOH/IPA	KOH/IPA	KOH/IPA
								30 min no Ag	30 min Ag	30 min Ag	30 min Ag	60 min no Ag	60 min Ag	60 min Ag	60 min Ag
Average reflectance	40.7	23.8	11.5	11.5	13.0	14.7	11.0	15.2	9.3	8.6	6.8	18.1	18.1	28.7	5.5
Samples	S16[a]	S17	S18	S19	S20	S21	S22	S23	S24	S25					
***p*-Si(111)**															
Etch *t* (min)	0	10	20	30	120	10	20	30	60	120					
Reductant[c]	NaOCl	Glu	Glu	Glu	Glu	AcA	AcA	AcA	AcA	AcA					
Average reflectance	40.4	15.1	15.5	10.2	9.6	13.6	7.7	6.5	9.1	16.7					

[a] S1 and S16 were processed using NaOCl solution before Ag particle deposition.
[b] S8 and S12 were texturized in KOH/IPA without Ag particle deposition.
[c] Glu = glucose, AcA = acetaldehyde.