Catalyst-referred etching of silicon

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Abstract

A Si wafer and polysilicon deposited on a Si wafer were planarized using catalyst-referred etching (CARE). Two apparatuses were produced for local etching and for planarization. The local etching apparatus was used to planarize polysilicon and the planarization apparatus was used to planarize Si wafers. Platinum and hydrofluoric acid were used as the catalytic plate and the source of reactive species, respectively. The processed surfaces were observed by optical interferometry, atomic force microscopy (AFM) and scanning electron microscopy (SEM). The results indicate that the CARE-processed surface is flat and undamaged.

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1. Introduction

The surfaces of semiconductor wafers for electronic devices are required to be flat and undamaged. Although there are numerous planarization techniques that are applied for many materials for various purposes, no technique enables the fabrication of flat and undamaged surfaces, simultaneously. For example, Si wafers are planarized by various methods, such as lapping, etching and chemical mechanical polishing (CMP). Lapping flattens the surface by abrasion with a hard flat polisher, but mechanical methods such as lapping causes increased surface damage. Such damage is removed by chemical methods like etching. However, chemical methods usually do not have planarization capability because the reaction is isotropic. They also cause etch pits depending on the surface defects that are present. CMP is applied as a surface-finishing method for electronic devices, but a disadvantage is the increased waviness due to elastic deformation of the soft pad.

We considered that a new efficient planarization of wafers should be capable of both making flat surfaces and chemical removal of surface damage. We proposed a new damage-free planarization method called catalyst-referred etching (CARE) \cite{1}. CARE was first used for silicon carbide planarization. The CARE-processed SiC surfaces are flat and undamaged compared with conventional CMP surfaces, according to the results of Nomarski differential interference contrast microscopy, optical interferometry, atomic force microscopy (AFM) \cite{1} and cross-sectional transmission electron microscopy \cite{2} measurements. The results showed that CARE has a high potential for SiC planarization and can be expected to be a planarization method of other materials as well. In this research, CARE was applied to Si planarization to achieve flat and undamaged surfaces. A Si (100) wafer and polysilicon (poly-Si) deposited on a silicon wafer were used as samples to investigate the performance of CARE on Si.
2. Experiment

2.1. Concept of care

CARE can flatten surfaces and remove surface damage chemically because the process is chemical etching, which should occur only near the flat surface of the reference catalyst. Fig. 1 shows the concept of CARE. First, the catalyst generates a reactive species. The reactive area is very thin to limit the reaction to near the reference catalyst surface. When the catalyst approaches the sample, the peaks are etched by contact with reactive species but the valleys are not etched because they are far from the reactive species. Ultimately, processed surfaces are made flat and undamaged, simultaneously.

To accomplish CARE, a catalyst and reactive species appropriate to the material being processed must be selected. We considered that F and OH radicals are capable removing Si and SiC because these species chemically remove Si in aqueous solutions [3,4] and SiC in plasma [5]. We performed an initial experiment in which a Pt wire was used as the catalyst that moved relative to and in contact with SiC in hydrogen fluoride (HF) solution. The results show that hard SiC can be removed. The reason for using Pt and HF is as follows: Pt has catalytic properties, such as the ability to dissociate various molecules [6] and the interaction between Pt surfaces and HF molecules in an aqueous solution can generate F and OH by self-dissociation.

2.2. Experimental setup and condition

Two apparatuses are prepared for local etching and for planarization. The local CARE apparatus has a catalytic rod in contact with the sample on a reciprocating sample stage. Poly-Si deposited on a silicon wafer was attached to the sample stage with a load of 50 g. The rod and sample were immersed in 2 mol/l hydrofluoric acid (Fig. 2).

The CARE planarization apparatus has a catalytic polishing pad made of Pt placed on a rotatable table. A wafer is fixed on the sample stage using wax and placed on the pad with a controlled pressure of 0.02 MPa, which is appreciably lower than that in conventional CMP. The polishing pad and sample were immersed in 2 mol/l hydrofluoric acid. The rotation speeds of the sample stage and pad were fixed at 6 and 7 rpm, respectively. Removal rates of approximately 1.0 μm/h can be obtained under such conditions. The sample wafers are p-type Si (1 0 0) wafers which have resistivities of 15.0–21.0 Ωcm. The processed surfaces were observed by optical interferometry, AFM and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Si (1 0 0) wafer surface

The surfaces of a CARE-processed Si (1 0 0) wafer and a commercial CMP Si (1 0 0) wafer were measured by optical
interferometry (Fig. 3) in a 64 × 48 μm area. The maximum
to or smaller than those on the CMP surface. The
The surface flatness was particularly improved compared with
The morphologies of the
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the conventional CMP surface. The morphologies of the
The P–V and RMS of the
Although a step-terrace structure was observed on
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The results indicate that the CARE reaction on SiC occurs only at step sites but that on Si occurs at both step and terrace sites. The optical interferometry results and AFM images indicate that CARE has a higher potential as a planarization method than the conventional CMP.

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some black areas were observed on the CARE-processed Si
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This is because a reaction between the Pt contaminant originating from the catalyst plate, the HF solution and the Si occurred during the CARE process. It has been reported that porous silicon was produced when a Si wafer with Pt particle deposition was immersed in a solution of H₂O₂ and HF [7–9]. Therefore, it is suggested that porous silicon was produced on CARE-processed surfaces. We investigated the processed areas by optical interferometry, AFM and SEM. The results reveal that the roughness deteriorated compared with other areas, however, no porous structure was observed. We concluded the porous Si was produced and etched by CARE simultaneously, thus no clear porous structure was observed. To planarize Si wafers without generating porous Si, a catalyst that activates only CARE must be selected.

3.2 Poly-Si surface

Poly-Si deposited on a silicon wafer was etched with a removal depth of 200 nm, using the local CARE apparatus. A SEM image of the CARE-processed surface is shown in Fig. 5. Some grain boundaries become irregular after CARE because of the gaps between the grains formed during poly-Si deposition, but grain boundaries without
gaps are flat. The results show that CARE yields a flat surface with only a minimum etching depth because only the topmost sites are etched without scratches or cracks being formed. The existence of some flat grain boundaries indicates that the occurrence of etching depended on whether the sample was near the catalyst.

4. Summary

The quality of CARE-processed Si (0 0 1) surfaces was evaluated by optical interferometry and AFM. The results indicated that the CARE-processed surface is flat. The SEM image of the CARE-processed poly-Si showed that CARE occurs only near the catalyst. CARE has a higher potential as a planarization method than conventional CMP.

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