Microelectronic Engineering 88 (2011) 3448–3451

Contents lists available at ScienceDirect

Microelectronic Engineering

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

The dry etching of TEOS oxide for poly-Si cantilevers in supercritical CO_2

Jae Mok Jung [a], Eunjin Yoon [a], Euesang Lim [a], Byung Chun Choi [b], Sang-Yong Kim [c], Kwon Taek Lim [a,*]

[a] *Department of Imaging System Engineering, Pukyong National University, Busan 608-739, Republic of Korea*
[b] *Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea*
[c] *Department of Semiconductor System, Korea Polytechnic College IV, Cheongju 361-857, Republic of Korea*

ARTICLE INFO

Article history:
Available online 9 December 2010

Keywords:
Etching
Sacrificial oxide
Poly-Si
Supercritical carbon dioxide
MEMS
Cantilever

ABSTRACT

Dry etching of *p*-tetraethylorthosilicate (TEOS) with HF/H_2O in supercritical carbon dioxide ($scCO_2$) was studied. The etch rate of TEOS increased with HF concentration and reaction temperature, while the concentration of H_2O and processing pressure were found to have little effect on the etch rate. Finally, poly-Si cantilevers with high aspect ratios (1:150) were released using this technique without stiction and residue on the surface.

1. Introduction

Silicon dioxide (SiO_2) thin films are widely used in the fabrication of microelectronic devices and micro-electromechanical systems (MEMS) as sacrificial layers. The wet isotropic etching process with aqueous hydrofluoric acid (HF) solutions is an effective way of etching the SiO_2 sacrificial layers as a fundamental step in the fabrication [1–3]. However, as the minimum feature size for industry requirements continues to shrink into the deep sub-micron region, the etching method using aqueous-based solutions has restrictions on the penetration into tiny features and also causes stiction of released parts on substrates or pattern leaning due to the capillary forces generated by the surface tension of a rinse liquid in the drying step. Techniques such as vapor HF systems, anhydrous HF gas-phase etching methods, and supercritical carbon dioxide ($scCO_2$) drying have been developed to resolve these obstacles [4–7]. $scCO_2$ has almost zero surface tension and does not generate a capillary force that causes stiction during drying. It is considered a dry solvent because it evaporates immediately from any surface or device at ambient temperature and pressure. Therefore, the $scCO_2$-based process eliminates the drying step, and prevents structural damage to materials in microelectronic devices. Recently $scCO_2$-based dry etching was widely reported using the HF/pyridine complex as an etchant [8–13]. Johns et al. obtained high etch rates of SiO_2 at low concentration of HF in pyridine/$scCO_2$ [1]. Malhouitro et al. investigated the impact of various processing parameters (HF concentration in $scCO_2$, processing temperature, etching time, fluid flow rate) on the etch rate of thermal SiO_2 using a HF/pyridine/$scCO_2$ mixture at a constant flow rate [10]. They found residue formation at the surface of the etched film, which was identified as SiF42 pyridine complex by FTIR analysis. More recently, the effects of process parameters as well as alcoholic co-solvents on the etch rate of various sacrificial oxides and etch selectivity have been studied in detail [11]. In this case, unwanted residues also remained after etching, therefore water-in-CO_2 microemulsions or bis(2-methoxyethyl)ether solution in $scCO_2$ were used to remove the residue after the etching process [12,13].

In this paper, the etching of *p*-tetraethylorthosilicate (TEOS) using HF/H_2O in $scCO_2$ was investigated for the purpose of residue-free dry etching. The effect of HF and H_2O concentration, processing temperature, pressure and time on the etch rate was studied. The release of polycrystalline silicon (Poly-Si) cantilevers with very high aspect ratios using this method was also reported.

2. Experimental

HF/H_2O (49 wt.% from Aldrich) diluted with DI water was used as an etchant solution. Carbon dioxide (99.99%, Dae Young Co.) was used as received. TEOS blanket wafers and polysilicon cantilevers of various lengths were fabricated for the etching experiment. For the blanket wafer, the low pressure tetraethoxyorthosilicate (LP-TEOS) whose thickness was 1080 nm was deposited on undoped silicon wafers. The poly-Si cantilever wafers were fabricated using a two-mask fabrication process. A 500 nm thick

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* Corresponding author. Tel.: +82 51 629 6409; fax: +82 51 629 6408.
E-mail address: ktlim@pknu.ac.kr (K.T. Lim).

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doi:10.1016/j.mee.2010.11.026

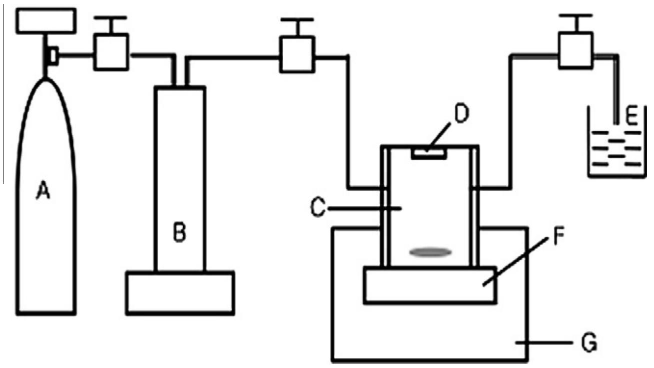

Fig. 1. Schematic representation of $scCO_2$ dry etching process. (A) CO_2 cylinder; (B) ISCO syringe pump; (C) sample chamber; (D) wafer; (E) 1 M NaOH solution; (F): electromagnetic stirrer and (G) heating fluid.

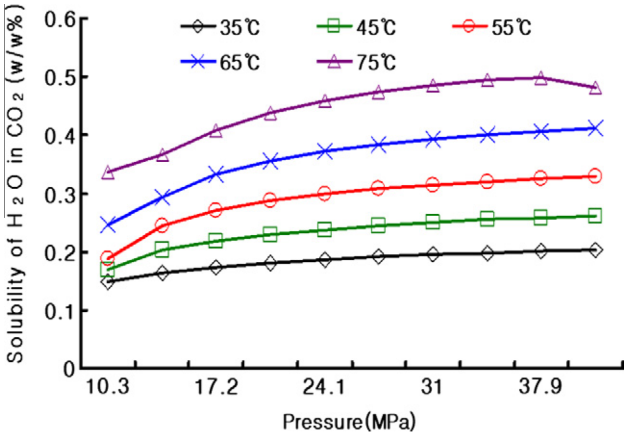

Fig. 2. Solubility of H_2O in CO_2 as a function of pressure and temperature.

sacrificial layer of low pressure tetraethoxyorthosilicate (LP-TEOS) was first deposited on (1 0 0) p-type silicon wafers. This layer was then dry etched down to the Si substrate using mask 1 to open the anchor areas for the poly-Si beams through a photoresist process. Subsequently, an undoped 300 nm thick poly-Si layer was deposited in an LPCVD reactor at 600 °C using SiH_4 gas. The test structures were finally formed with mask 2 by reactive ion etching (RIE) of poly-Si in a similar manner to the previous step. The cantilevers have a width of 1.25 μm with a length increment of 1.25 μm. The thickness of the polysilicon structural layer is 300 nm, and the space between the beam and substrate, defined by the thickness of the sacrificial layer TEOS is 500 nm. The wafers were cleaved into 1×1 cm^2 samples before use.

An HF-compatible jacket type one-chamber etching apparatus was used for the dry etching experiment as depicted in Fig. 1. The temperature of the chamber was maintained by circulating water from a temperature-controlled water bath (G). The cap of the chamber (C) was closed quickly after the etchant solution was injected in the etching chamber equipped with a magnetic stir bar. A wafer piece (D) was previously attached on the bottom of the cap by a carbon adhesive tape. Immediately afterward, densified CO_2 was introduced into the chamber at 13.8 MPa by a syringe pump (B) (ISCO 260D). A screening tripod was installed over the magnetic stirred bar and the time interval between the etchant injection and CO_2 pressurization was kept below 20 s in order to reduce unfavorable pre-etching. The etchant solution was stirred for a desired period before the chamber was flushed with pure $scCO_2$. The flow rate of pure CO_2 was maintained at 30 mL/min for 5 min at the same pressure (13.8–31 MPa). A 1 M NaOH solution (E) was used to neutralize the HF solution which was discharged after the etching reaction. Etching experiments were carried out at different HF concentrations, temperatures, and pressures.

The thicknesses of TEOS thin film before and after etching were measured with a spectroscopic ellipsometer (J.A. Wallam. Co. M2000D) using single cauchy model and normal SiO_2 fitting. The mean square error was maintained below 50. Five different points were measured to calculate an average thickness of each sample. The released cantilevers were observed using a scanning electron microscope (SEM, HITACHI S-2700).

3. Results and discussion

3.1. The dry etching of TEOS with $HF/H_2O/scCO_2$ solution

The HF aqueous solution (49 wt/wt.%) was further diluted in DI water before using it as an etchant. It is known that bulk CO_2 dissolves a certain amount of water [14]. Fig. 2, where the data were come from our experimental data base, represents the solubility of water-in-CO_2 as a function of pressure at different temperatures, for example, the solubility of water-in-CO_2 is approximately 0.14 wt.% at 27.6 MPa and 35 °C. Therefore the etching experiments were performed at a concentration lower than the saturation point taking into account the water produced as a side product. The system was maintained as a homogeneous solution of HF/H_2O in $scCO_2$. The homogeneity was confirmed by visual observation through a sapphire window at the reaction condition. After the reaction, the solution was replaced with $scCO_2$, and this could exclude water pool from the process solution and eliminate the capillary force during drying. Interestingly, this process did not produce any CO_2 insoluble residue which was always observed in HF/pyridine based dry etching.

Prior to systematic investigation of $HF/H_2O/scCO_2$ dry etching, the etch rate was compared with that of the conventional wet etching. About 0.0025 g of HF was used as an etchant in a 20 mL of $scCO_2$ solution for the $HF/H_2O/scCO_2$ etching, while 0.025 g of HF and 0.0125 g of HF with 0.0125 g NH_4F were used in 20 mL water solutions for the HF/H_2O and $HF/NH_4/H_2O$ etching, respectively. As shown in Fig. 3, the etch rate of the TEOS wafers in $HF/H_2O/scCO_2$ was much higher than the HF wet etching performed in water (including a NH_4F buffered solution). The difference between the etch rates increased with reaction temperature (35–65 °C). Since $scCO_2$ has liquid-like density and gas-like viscosity the higher etch rate in $HF/H_2O/scCO_2$ compared with the HF/H_2O wet system may be due to the higher diffusion of etchant molecules in supercritical CO_2. The etch rate of $HF/H_2O/scCO_2$ was also found to be higher than that of HF/pyridine/$scCO_2$ at similar HF concentration (25 μm vs. 29 μm) (see Fig. 4). It is considered that the relatively lower etch rate of HF/pyridine/$scCO_2$ system is partly attributed to the residues deposited at the surface of the film which limits the etching reaction [10].

The etching experiment was performed over a period of 8 min at 13.8 MPa and 50 °C with 25 μM of HF in 10 mL $scCO_2$. It is found that the mean etch rate is almost constant after 3 min of reaction time as shown in Fig. 5. The initial mixing in the etching chamber caused a slight increase in the etch rate at the earlier time. In other words, the mean etch rate was found to be lower at 2 min reaction time possibly due to insufficient initial mixing of the etchant in the chamber. After enough time to get a homogeneous etchant solution, the mean etch rate became almost constant over the reaction time, which is in accordance with the trend in HF/H_2O based wet etching [4]. The trend contrasts with that of HF/pyridine system where the instantaneous etch rate decreased as processing time increased due to the etching residue formation [8,10].