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RESEARCH ARTICLE

The role of silanol groups on the reaction of SiO_2 and anhydrous hydrogen fluoride gas

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Abstract

It is essential to etch SiO_2 for producing silica glass components, semiconductor devices, and so on. Although wet-etching with hydrogen fluoride (HF) solutions is usually employed for this purpose, it faces a drawback that microstructures stick during the drying of the solution. To overcome this problem, we have developed a dry-etching technique with gaseous HF at high temperatures. In the present study, an interesting phenomenon was found that silicon thermal oxides were much less etched than vitreous silica by gaseous HF. Such difference had not been found in wet- or humid HF gas etching. Because their bulk chemical formulae are the same (SiO_2), it was suggested that the surface species affected the reaction rate. In fact, preprocessing with water vapor plasma remarkably increased the etching rate on the thermal oxides layer, and vacuum heating almost completely suppressed the reaction on the vitreous silica and the plasma-treated thermal oxides. These results indicate that the surface silanol groups enhance the reaction between SiO_2 and gaseous HF. Based on the results, a model of chain reaction for SiO_2 and gaseous HF was proposed, where the surface silanol groups act as the reaction center.

KEYWORDS

etchants/etching, silica, surface modification

1 | INTRODUCTION

Amorphous silicon oxide (SiO_2) is widely used in industry. For instance, oxide layers on silicon wafers are inevitable for producing semiconductor devices such as integrated circuits and microelectromechanical systems (MEMS),[1–4] where the oxides are utilized as an insulation layer and/or an etching-stop layer. Applicative use of vitreous silica is also extensive such as photomasks and gratings thanks to its high transmittance in the ultraviolet region and/or the low coefficient of thermal expansion.[5,6] In the production of these components/devices, it is desired to etch SiO_2 with a simple, inexpensive, and quick way. The use of the effective and controllable etching technique is especially important for producing small and/or high-performance devices.

SiO_2 is usually etched with a reactive ion etching technique or wet-etching with hydrogen fluoride (HF) solution.[1–3,7–10] However, the former has disadvantages in throughput because it requires a vacuum and it can

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