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Characterization and removal of polysilicon residue during wet etching

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ABSTRACT

Process optimization of polysilicon removal by wet etching with alkaline chemicals in a gate-last device integration scheme was investigated. Initial surface condition of the polysilicon layer, spreading properties of wet etching chemicals, and generation of hydrogen bubbles during wet etching were revealed as key parameters affecting the degree of polysilicon residue after wet etching both in patterned structures and on non-patterned bare wafers. Wet etching starting from a hydrophilic polysilicon surface showed successful polysilicon removal (no residues) compared with a hydrophobic polysilicon surface, indicating that the spreading and wetting properties of the wet etching chemical on polysilicon surface is very important in the polysilicon wet etching process. Therefore, it is believed that chemicals showing lower contact angles on the polysilicon surface may be suitable to enhance process efficiency. Furthermore, hydrogen gas generated during silicon wet etching can hinder polysilicon removal, causing significant residues after processing. Ultrasonication or addition of IPA in the wet etching solution can be an alternative method for preventing the hydrogen bubble effect.

1. Introduction

The introduction of high-k/metal gate into manufacturing has enabled the continuation of device scaling and Moore's law [1–3]. Two main approaches are applied for metal gate integration toward achieving ultra-thin electrical oxide thickness (EOT): gate-first and gate-last integration schemes. The latter broadens the range of material options for effective work function tuning by allowing a low thermal budget after metal deposition (decoupling it from junction activation), while the smallest EOTs reported to date have been demonstrated with a gate-first scheme [4,5]. One of the most important processes in the gate-last scheme is replacement of the polysilicon gate (RPG) step, which has been extensively investigated for the incorporation of high-k/metal gates into 45 nm node and beyond technologies. In process flow, polysilicon is deposited first as a dummy material to be removed later by wet processes. The space left by polysilicon is then refilled with a high-k dielectric and a metal gate [6]. Complete removal of the dummy polysilicon layer with high selectivity to the gate oxide is required for the normal operation of a transistor and improvement of yield. However, it is getting more difficult to eliminate the dummy polysilicon in very confined gate areas with the continuous down scaling of feature size and increased aspect ratio required in the metal gate integration strategy. To be able to control the process of polysilicon removal, a detailed understanding of interfacial characteristics and reaction mechanisms is essential.

The key factors in this process are as follows: ① complete removal of the polysilicon without residue, ② no damage to the gate oxide underneath the dummy polysilicon, and ③ high etch selectivity to gate spacer (Si_3N_4) or inter layer dielectric (ILD) oxide, as shown in Fig. 1(c). Generally, a dry etch process would not be preferred for the removal of a dummy poly gate, since it would damage the oxide gate. Therefore, polysilicon is commonly wet etched by ammonia chemistry such as dilute ammonia, tetra methylammonium hydroxide (TMAH), and tetraethylammonium hydroxide (TEAH). The most critical issue in this wet process is unremoved polysilicon residues found in the confined space between patterns or the inner corner area of the gate bottom, even though a very long wet etching time would be required, since transistor performance and chip yield are greatly influenced by polysilicon residues remaining inside the gate structure. These kinds of polysilicon residues can be affected by various factors including polysilicon morphology and crystal orientation, wet etching chemicals and process conditions, dopant diffusion into the dummy poly gate, heat treatment, and pattern structures [7,8].

The gross reaction of silicon wet etching in an alkaline solution suggested by Seidal et al. is as follows, showing that the hydroxide ion is the main etching species and hydrogen gas is produced as a byproduct [9].

$$Si + 2OH^- + 2H_2O \rightarrow SiO_2(OH)_2^{2-} + 2H_2\ (g) \quad (1)$$

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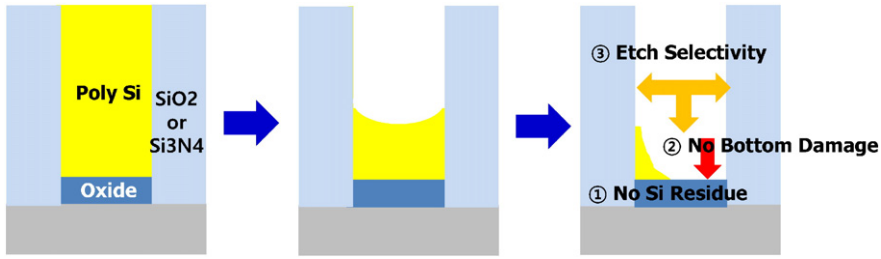

Fig. 1. Schematic process flow and key factors affecting polysilicon wet etching step.

From this simplified chemical reaction, wet etching of silicon seems to be indifferent to the source of the hydroxide ion, whether ammonium hydroxide (NH_4OH), TMAH, or TEAH. However, the wet etching process of polysilicon in large-scale 300 mm wafer manufacturing shows a strong dependence on wet process conditions like pre-treatment of the polysilicon surface before the main wet etching process and the kind of alkaline etching chemicals (having different cationic species). This is especially true in the results of polysilicon residues after replacement of the poly gate process. This means that not only the amount of etching species (hydroxide ion), but also the wettability of wet etching solutions on the polysilicon surface are affected by counter ions. Further, the surface properties of polysilicon and the presence of hydrogen gas also play an important role in complete polysilicon removal inside dummy gate structures. In particular, reports on the effect of hydrogen gas, generated during reaction on the polysilicon removal in RPG process are very rare, because the detection of polysilicon residue by hydrogen bubbles is not easy in the semiconductor manufacturing process.

In this study, characteristics of the polysilicon removal in polysilicon wet etching were investigated, especially in terms of the surface states of initial polysilicon, wet etching conditions, and wetting properties of chemicals. Wettability of different wet etching chemicals on a polysilicon surface was evaluated with the measurement of contact angle (CA). Additionally, the effect of hydrogen gas in this process was first monitored in 300 mm wafer inspection, and the evolution of hydrogen gas/removal method on the wafer surface was investigated.

2. Experimental

2.1. Wafer processing and inspection method

Fig. 2 shows a typical polysilicon wet etching process in a single wet station with a 300 mm wafer, including several sub-steps of the wet process. (a) First, a native oxide on a polysilicon surface should be removed by the treatment of diluted HF (dHF), since most wet etching chemicals for polysilicon show high etching selectivity to silicon oxide. (b) After sufficient wet etching chemicals such as hot ammonium hydroxide solution or TMAH are applied onto the polysilicon layer, and (c) the wafer is rinsed with deionized water (DIW) and dried by spinning at high rpm.

The locations of defects after polysilicon wet etching were inspected by using PUMA (KLA-Tencor, patterned wafer inspection) and a Surfscan SP2 (KLA-Tencor, non-pattern wafer inspection). The minimum defect size that SP2 can detect is 45 nm, and close examination of individual defects was performed with a high resolution scanning electron microscope (SEM, Hitachi). All bare wafers, which showed less than 50 initial defects, were used in the experiment to increase accuracy of defect counts and ensure the reliability.

2.2. Contact angle measurement

CA measurement was carried out with a SL150 static optical contact angle goniometer from Kino by using the sessile drop method. In the measurement of CA, 2 cm × 2 cm polysilicon coupon wafer pieces were prepared by cutting a 300 mm wafer deposited with 2000 Å of a polysilicon layer. In contrast to ordinary CA measurement methods that use DIW as a standard droplet, wet etching chemicals such as NH_4OH, TMAH, tetrabutylammonium hydroxide (TBAH), and a mixture of isopropyl alcohol (IPA) and TMAH were dropped onto the prepared wafer surface for direct comparison of surface wettability of each chemicals on the polysilicon surface. For this purpose, CAs were monitored after each step of the polysilicon wet etching process as follows: ① as-prepared polysilicon layer with 2000Å thickness, ② after dHF pre-treatment, and ③ after standard clean 1 (SC1) treatment (SC1 treatment was applied for the modification of polysilicon surface from hydrophobic, after HF treatment, to hydrophilic). Then, 12 μL droplets of each etching chemical with the same concentration were dropped by microsyringe with a needle. All measurements were carried out within 30 min after chemical preparation to minimize the change in surface state by exposure to atmosphere. Each CA reading was averaged from at least 5 measurements.

2.3. Investigation of hydrogen bubble generation and its removal method

Further, 6 wt.% of TMAH (60 °C) was used as a basic wet etching solution for the confirmation of hydrogen gas generation during polysilicon wet etching. After a 2 × 2 cm Si wafer piece was immersed into a beaker containing TMAH (Table 1, condition 1), the generation of hydrogen bubbles was observed by using a commercial optical camera in the darkroom with laser light. For the removal of bubbles on a Si wafer, various kinds of physical and chemical approaches such as simple magnetic stirring, 300 MHz of ultrasonication and addition of IPA into TMAH etching solution were used, as summarized in

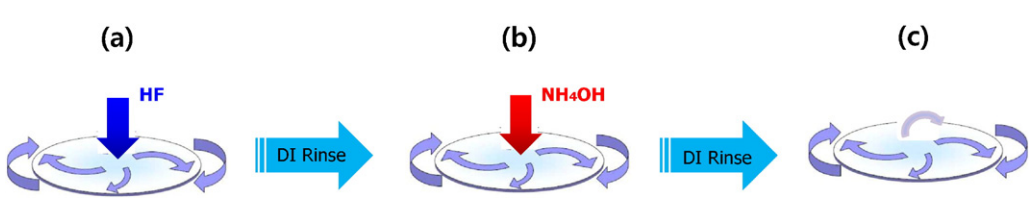

Fig. 2. General process sequence of polysilicon wet etching process in single tool: (a) HF treatment for the removal of native oxide, (b) polysilicon wet etching by ammonium hydroxide, and (c) final DIW rinsing and spin drying.