Mechanochemically Enhanced Selective Material Removal during poly-Si CMP by Nanocontact-induced Dissolution

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INTRODUCTION

The shallow trench isolation (STI) method has been improved for advanced, multi-level cell NAND-flash memory device manufacturing.[1] The chemical mechanical polishing (CMP) process is adopted to planarize polycrystalline silicon layers deposited on active region surfaces of wafers. In this process, the high removal rate of poly-Si and high selectivity of poly to oxide was required. Generally, high solid contents are needed to improve the removal rate, however, it cannot be possible to escape the particle defect on the wafer surface during or after the CMP process. When the polymeric chemical was added to the slurry for selectivity control, the organic residue was left on the surface of the wafer resulting in a cleaning issue in the post-CMP process. Thus, future-oriented STI CMP slurry will be required to contain low solid and chemical contents.

BACKGROUND

When pressure is locally loaded on the substrate, the structure of silicon is distorted resulting in the occurrence of densified area. In this area, because the bond strength between atoms becomes weak and unstable, it is possible to be attacked by chemicals easily. From the Arrhenius kinetics model, the dissolution energy and bond strength drastically decreased when the force was loaded on the Si bonds. [2]

$$V = D_e \left(1 - e^{\left(\frac{-2F_{max}}{D_e} x \right)} \right)^2 \tag{1}$$

$$E_A(x_a) = V_{eff}(x_{TS}) - V_{eff}(x_a) - \frac{1}{2} h A(x_a) \tag{2}$$

The Morse potential, V, decreases as the external force, F, is applied, in which the bond is elongated by an amount x_a. The local maximum $V_{eff}(x_{TS})$ corresponds to the transition state of the bond rupture event. For the frequency factor $A(x_a)$, the activation energy, E_A, is calculated as Equation (2). The kinetic analysis implies that the lifetime of the bond varies as a function of the applied force. When the Si bonds got weak, the substitution reaction was activated to form Si-F bonds. Then the crystalline structure of poly-Si becomes distorted, which weakened the Si bond strength. If the mechanical stress is loaded on the poly-Si surface, a decrease in bond energy leads to activation of substitution reaction. Then the Si bonds under the Si-F layer got distorted, therefore, the mechanical abrasion of abrasives got enhanced. From this conceptual mechanism, we could expect high CMP performance with a low concentration of solids and chemicals.

EXPERIMENTAL

In this experiment, the load pressure on pad asperity, load force on each particle, and indentation depth are calculated based on contact mechanics. The weakened structure of poly-Si when certain forces are applied to the wafer was verified by atomic force microscopy (AFM). The rounded tip of SiO$_2$ with 30 nm of front-end radius is used to apply force in accordance with the silica nano-abrasives. Tetrabutylammonium fluoride (TBAF) was used as an additive, providing fluoride species.

DISCUSSION

The pressure on pads asperity and particles can be obtained according to Hertz theory and contact mechanics. [3] The properties of the IC1010 polyurethane pad were adopted as parameters for calculation, and the 30 nm-sized silica nanoparticles with solid contents of 0.1 wt.% were reflected. When 2 psi of normal pressure is applied, the pressure transferred from pad asperity to wafers is 0.86 MPa and the pressure from a nanoparticle on top of this asperity is 148 MPa. The contact force converted from this pressure is 134 nN, and the depth at which the particles are pressed into

the wafer is 3.4 Å for the poly-Si film as shown in Fig. 1. The calculated force on the particle was set at the magnitude of the force on the tip in AFM.
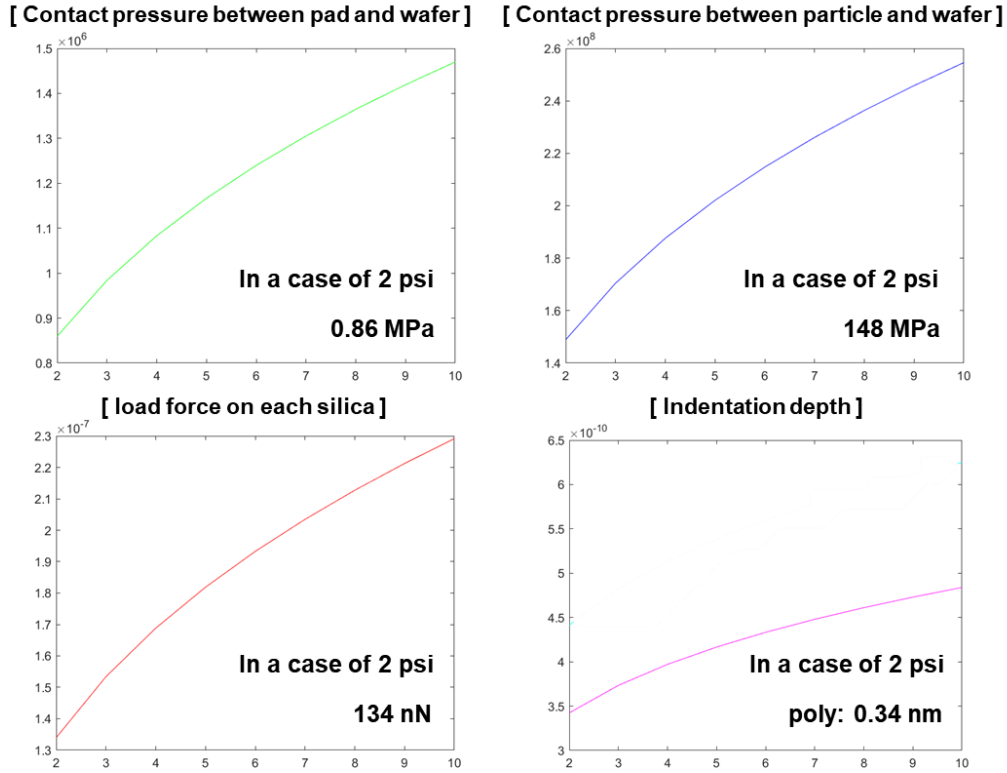

Fig.1 Calculated contact pressure, load force, and indentation depth based on the Hertzian model.

The AFM measurement verified the reaction of fluoride ion from TBAF with poly-Si in an aqueous environment as shown in Fig. 2. The wafer was scratched as the 5 × 5 μm^2 areas once by applying 134 nN of force to the tip within different solutions. There was no abrasion in DI water when the tip scratched the wafer, but it is possible to confirm the material removal in the TBAF solution. The absence of static etch of poly-Si in TBAF solution makes sure that the results of material removal were caused by nanocontact-induced dissolution. From the Arrhenius equation, the etch reaction hardly occurs in a very low concentration of etchant because of high activation energy. Finally, the results show that the tip could wear the wafer even though not enough force was applied because the crystalline structure of Si bonds collapsed under the influence of TBAF.

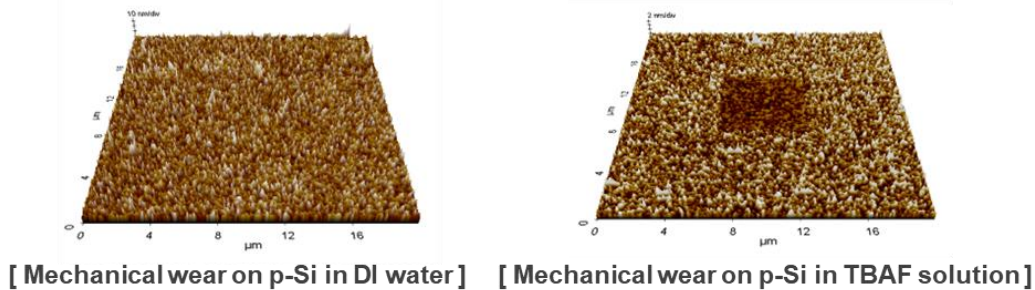[Mechanical wear on p-Si in DI water]   [Mechanical wear on p-Si in TBAF solution]

Fig. 2 AFM results of mechanical stress on poly-Si in different solutions.

When only 0.1 wt.% of abrasives are used or when only 2 mmol of TBAF are contained, the amount of material removal was hard to find. However, when both are used, the removal rate drastically increased. According to an

increase in the concentration of TBAF, the removal rate of poly-Si increased. The mechanical stress loaded on the poly-Si surface decreases in bond energy leading to activation of substitution reaction. Therefore, the Si bonds under the Si-F layer got distorted, in which the mechanical abrasion of abrasives got enhanced. In addition, the OH$^-$ ion also acts as F$^-$, which dissolute the Si atoms. Both species of solely OH$^-$ and F$^-$ ion dissolute the poly-Si and the removal rate of poly-Si is high in alkaline solution compared to acidic conditions.

On the other hand, the SiO$_2$ film, which is hydrated and forms a silanol group on the surface, reacts with HF^{2-} or H$_2$F$_2$ to form a Si-F bond. When Si-F is created, the three subsequent nucleophilic alternative reactions proceed very quickly, breaking the Si-F unit from the SiO$_2$ matrix. The cut-off position returns to its initial surface state and the previous reaction proceeds again. The OH$^-$ group is a difficult group to fall apart from silanol and needs external help to eliminate them. Here, H$_2$F$_2$ and HF^{2-} can help eliminate OH$^-$. It can be helped by the OH side of the silanol group and the interaction of the part-parallel F-H coordination. This behavior allows the second F of H$_2$F$_2$ and HF^{2-} to come close to the silicon atom. These elimination and addition reactions can occur continuously. Additionally, monofluorides such as HF and F$^-$ cannot perform this reaction. However, most fluoride ion exists as monofluoride in alkaline solution based on equilibrium models. These are the reasons why there is still no removal rate for oxide in alkaline slurry. For the oxide removal, the HF^{2-} and H$_2$F$_2$ species must be considered. Moreover, the electrostatic repulsion between silica and the oxide wafer increased by strongly charged negative zeta potential, which hinder the physical contact between them. The poly-Si film could escape that hindrance because it maintains its isoelectric zeta potential whether the pH is changed.
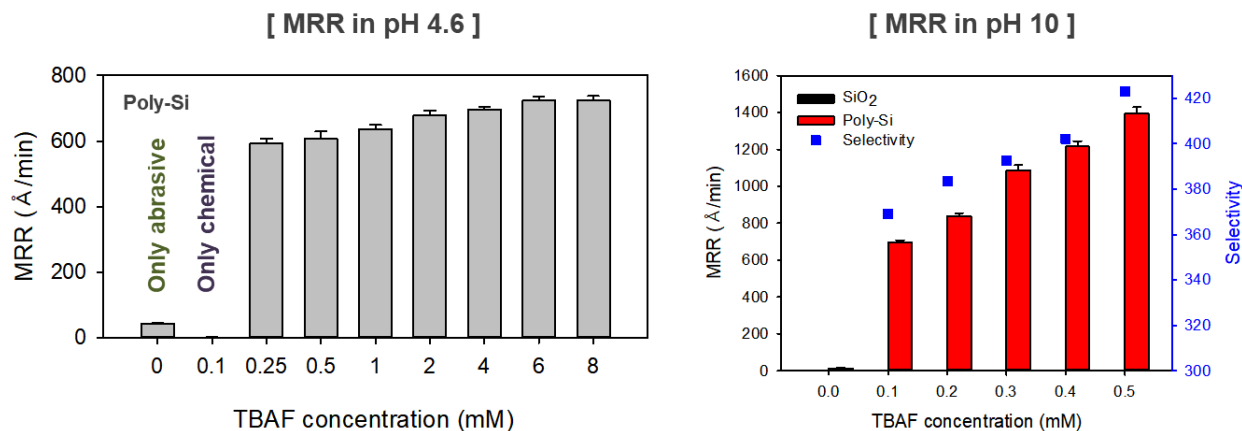

Fig.3 MRR according to the concentration of TBAF and pH

CONCLUSIONS

In order to achieve the isolated poly floating gate, the poly-Si to oxide removal selectivity is the most important factor for the poly isolation CMP process. The slurry for poly-Si CMP usually contains hazardous and lots of chemicals and abrasives to achieve a high removal rate and selectivity. It is a challenge to develop a kind of novel chemical mechanical polishing slurry of high polishing performance with environment-friendly compositions. In this study, a semi-abrasive free slurry was developed by utilizing the mechanism of nanocontact-induced dissolution that the Si-Si bond is weakened by physical forces then substitution ion easily penetrates the Si structure. The developed slurry is composed of over 99.8% of water which is eco-friendly. 50 times enhanced MRR and fully selective polishing with over 420 selectivity ratio were achieved by using the nanocontact-induced dissolution and selective substitution reaction, although the slurry contains very few chemicals and abrasives.

REFERENCE
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