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ScienceDirect

Scripta Materialia 59 (2008) 1178 1181

Scripta MATERIALIA

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Damage-free polishing of monocrystalline silicon wafers without chemical additives

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Received 14 July 2008; revised 24 July 2008; accepted 2 August 2008
Available online 19 August 2008

This investigation explores the possibility and identifies the mechanism of damage free polishing of monocrystalline silicon without chemical additives. Using high resolution electron microscopy and contact mechanics, the study concludes that a damage free polishing process without chemicals is feasible. All forms of damages, such as amorphous Si, dislocations and plane shifting, can be eliminated by avoiding the initiation of the β tin phase of silicon during polishing. When using 50 nm abrasives, the nominal pressure to achieve damage free polishing is 20 kPa.

Keywords: Silicon; Damage free; Polishing; Chemicals; Stress

The semiconductor industry requires silicon wafers with super-finished surface and damage-free subsurface [1]. Hence, understanding the deformation mechanisms in monocrystalline silicon during surface processing has been a research focus [2]. Molecular dynamics analysis shows that amorphous layer formation occurs during two-body contact sliding, but can be avoided in three-body polishing [3]. Meanwhile, experimental studies indicate that phase transformations in silicon are complex, and are related to many factors, such as the hydrostatic and deviatoric nature of the stress state and the loading/unloading rates during surfacing [4 10].

Currently, chemical mechanical polishing (CMP) processes are most common for final stage surfacing of monocrystalline silicon wafers in production [11,12]. In a CMP, material removal is coupled process of chemical reaction and mechanical removal, in which the chemical reaction is to weaken the atomic bonding of the surface silicon atoms with the substrate so that the mechanical removal can take place without altering the crystal lattice in the subsurface, and hence achieving a damage-free polishing. However, in CMP, chemical additives such as acetic acid, glycine, ethylenediamine and citric acid with hydrogen peroxide are required. Some of these chemicals are toxic, and proper decomposition after CMP are essential [13,14]. This increases production cost and creates disposal issues of the toxic chemicals. A natural question is therefore: Is it possible to realize damage-free polishing without chemical additives?

It is known, according to a series of theoretical and experimental investigation [2 6,15,17] that in polishing a silicon wafer abrasive particles in the polishing slurry interact with the silicon, leading to surface material removal and irreversible subsurface deformation. As a result, the silicon's atomic lattice in the subsurface is altered and significantly damaged, e.g. multiple phase transformations [2,15,17], dislocations [2,6,18] and stacking faults [2,15]. It has been understood through extensive studies of nano-/micro-indentation and scratching that the magnitude of forces, on silicon by an abrasive particle is critical to microstructural changes in the subsurface. A small force causes an amorphous phase change and some stacking faults, but a greater force can further introduce dislocations, R8/BC8 phases and cracking [2,15,17]. Theoretically, it has been found that the β-tin phase of silicon during the abrasive loading plays a pivotal role in the microstructural formation [2 5]. In a two-body contact situation [4 5], i.e., when the abrasive is without a rotational motion in its interaction with the silicon wafer, if the stress caused by the abrasive loading can be smaller than the threshold of β-tin formation, subsurface damage in silicon will not occur after the abrasive particle moves away. In a three-body contact situation [3], i.e., when an abrasive

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doi:10.1016/j.scriptamat.2008.08.002

has both rotational and translational motions, the adhering mode of material removal will leave a perfect subsurface of silicon. These theoretical studies indicate that a damage-free polishing is possible without using the chemicals of CMP processes, if we can control the interaction stresses between abrasives and silicon during a polishing operation to make sure that the β-tin phase is not initiated.

This letter explores experimentally the possibility of damage-free polishing of monocrystalline silicon without using any chemicals. Experiments were conducted on commercial (100) silicon wafers, using Logitech PM5 Auto-Lap Precision Lapping/Polishing Machine. The abrasives were aluminum oxide, at three average grain sizes of 15 μm, 300 nm and 50 nm. The polishing conditions used are summarized in Table 1. When the abrasive size is larger, the average number of abrasives in a unit area of polishing is less when the weight percentage of abrasives in the polishing slurry is same. Therefore, when larger abrasives are used in polishing, the abrasive silicon interaction force is greater, and *vice versa*.

The microstructures of the specimens' subsurface after polishing were studied using a high resolution transmission electron microscope (HRTEM), JEOL JEM-3000F, operating at 300 kV. All transmission electron microscopy (TEM) studies were performed on cross-section view samples. The <110> cross-section TEM specimens were prepared by an improved technique using a tripod [15]. During sample preparation, temperature was kept below 100 °C to avoid any structure alterations. Further, coefficients of friction between abrasives and silicon were measured after various polishing time, for 50 nm abrasive at 20 kPa pressure and 1 mm/s sliding velocity, using a modified Universal Tribometer.

Figure 1 shows the effect of abrasive size on the microstructural changes in the subsurface of silicon after polishing. It is clear that the depth of amorphous transformation increases with increasing abrasive size, i.e., with increasing the force magnitude on a single abrasive. This is consistent with the theoretical predictions [3 5,16]. Further, other types of stress-induced damages to the silicon crystal are also observed after polishing using 15 μm and 300 nm abrasives. Dislocations (Fig. 2a) and plane shifting (Fig. 2b) appear below the amorphous layer (in Zones {1} and {2} of Fig. 1a). It seems that shear stresses on the {111} slip planes may be the driving force for the formation of these dislocations [8].

Figure 1b shows a cross-section of a nano-scratch by a 300 nm abrasive, where the interface between the amorphous and the parent silicon is irregular. The lattice structure of the material at the interface in region {1} (Figs. 1b and 3) is different from the original

Table 1. Summary of polishing conditions

Abrasive size [μm]	Nominal pressure [kPa]	Speed [m/s]	Polishing time [min]	Total removal (±0.05) [μm]
15	37	0.172	60	24.07
0.3	37	0.172		10.37
0.05	79	0.143		13.73
	37	0.172		10.57
	25	0.143		8.95
	20	0.143		7.63

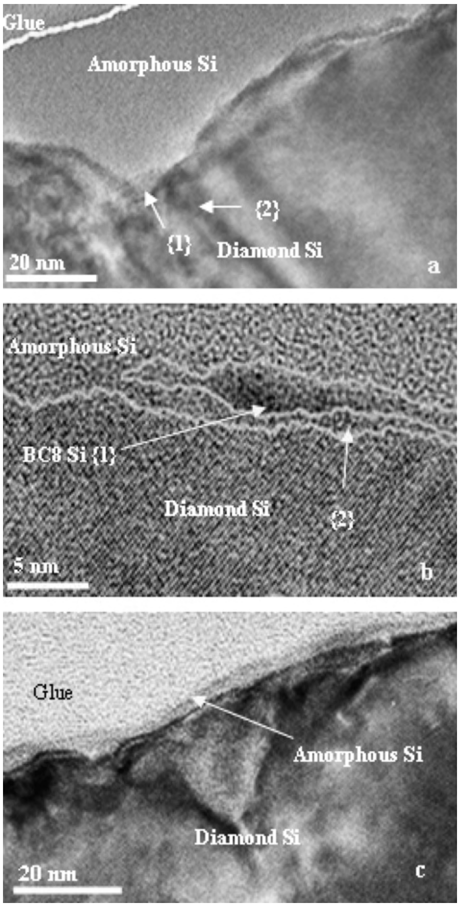

Figure 1. Cross sectional HRTEM images of polished silicon using (a) 15 μm, (b) 300 nm and (c) 50 nm abrasives at a nominal pressure 37 kPa.

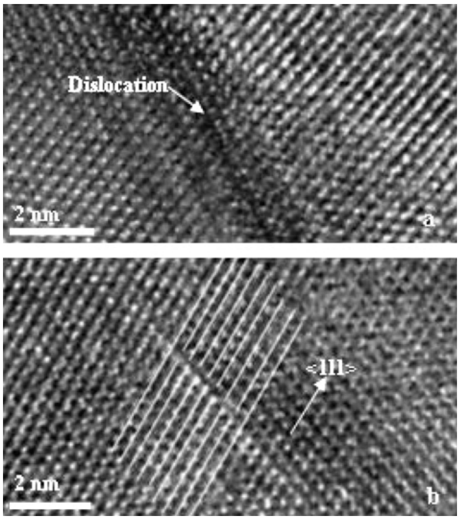

Figure 2. HRTEM images in [110] orientation of polished silicon, showing defects produced by 15 μm abrasives: (a) Dislocation and (b) plane shifting.

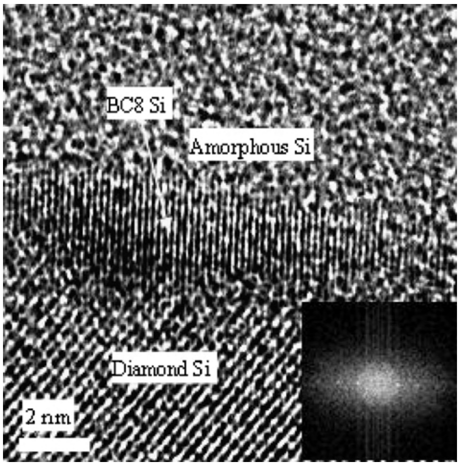

Figure 3. Higher magnification image of region {1} in Figure 2b. (Inset is the image from FFT analysis of the crystal structure at the interface between the parent silicon crystal and the amorphous phase).

diamond structure of silicon. A fast Fourier transform analysis suggests that in this region a BC8 phase (Si-III) [8 10,17,19] has formed. Further, the interface at region {2} (Fig. 1b) contains a narrow band of amorphous silicon just above the original silicon structure. The formation of this amorphous band is due to the β-tin phase formation during loading in polishing, which is consistent with the theoretical predictions [4 5] and experimental findings [15].

When the load decreases, the structure above the interface becomes entirely amorphous. As shown in Figure 1c, a smooth, uniform amorphous layer is generated by polishing using 50 nm abrasives. This concludes that unlike polishing by large abrasives, nano-abrasive polishing does not generate R8/BC8 phases and dislocations, confirming that a reduction in magnitude of the force on a single abrasive reduces the degree of subsurface damage.

When the magnitude of the abrasive-silicon interaction forces is reduced, by decreasing the nominal polishing pressure to 25 kPa using 50 nm abrasives, Figure 4a, the amorphous layer almost disappeared, with only a few isolated amorphous pockets. With a further reduction in pressure to 20 kPa, we achieve a damage-free polishing without the need for any chemical additives, Figure 4b.

The mechanism of the above damage-free polishing can be explained by the stress-dependent phase transformation activities in silicon. According to Refs [2 5], if the octahedral shear stress, σ_{oct}, in the neighborhood of an abrasive-silicon contact zone is above 4.6 GPa, but the corresponding hydrostatic stress, σ_{hydro}, remains below 8 GPa [2], then the material removal will take place without the formation of β-tin phase of silicon. As a result, when the abrasive slides away, the silicon substrate after unloading will recover entirely to its original crystalline structure without any residual damage.

To verify this, let us consider an individual abrasive-silicon interaction during polishing as a contact sliding with friction. The location at which the critical condition ($\sigma_{oct} > 4.6$ GPa, $\sigma_{hydro} < 8$ GPa) occurs depends on the friction coefficient, μ, between the abrasive and the surface according to contact mechanics. When μ approaches around 0.5 [20], such critical stress condition will be reached in the neighborhood of the abrasive silicon contact zone. Figure 5 shows our measured friction coefficient during polishing (abrasive size 50 nm, polishing pressure 20 kPa), which indeed demonstrates that μ is around the critical value, verifying that the above material removal mechanism takes place in the mechanical damage-free polishing process leading to the result of Figure 4b.

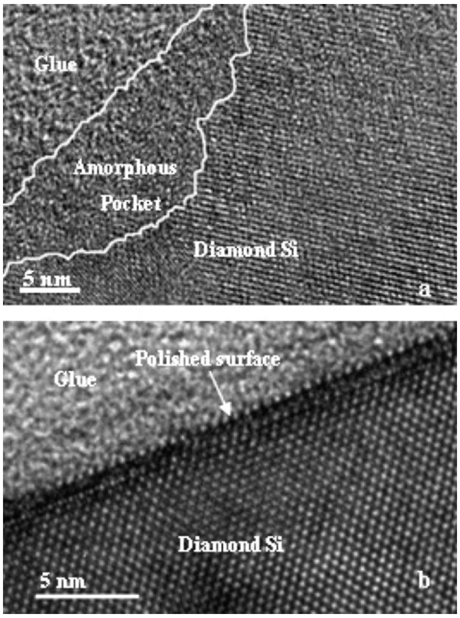

Figure 4. Cross sectional HRTEM images due to various pressures: (a) 25 kPa and (b) 20 kPa.

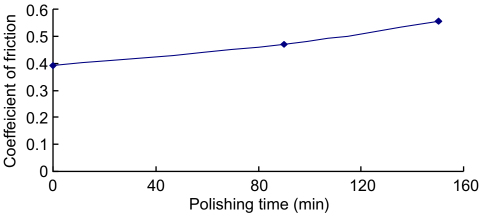

Figure 5. Coefficient of friction between abrasives and silicon with 50 nm abrasive particles.

To understand the loading/contact condition of a single abrasive under such critical polishing condition will help the design of damage-free polishing using different abrasive sizes and polishing pressure. According to contact stress analysis [20], the critical friction coefficient above corresponds to $\sqrt{J_2}/p_o$ 0.4, where J_2 is the second stress invariant, and p_o is the maximum surface pressure due to Hertzian contact loading. Note that

$$\sigma_{oct} = \frac{1}{3}\sqrt{2J_1^2 - 6J_2},$$

where

$$J_1 = 3\sigma_{hydro}.$$

Substituting the critical values of σ_{oct} 4.6 GPa and σ_{hydro} 8 GPa [2] into the above equations, we obtain the critical maximum contact pressure p_o, below which damage-free polishing of silicon is possible. Then, from the classical contact mechanics [21], we get the critical abrasive silicon interaction force $P \leqslant 2.97\ \mu\text{N}$, Hertzian contact radius $a \leqslant 6.69$ nm and abrasive penetration depth $\delta \leqslant 1.78$ nm (Young's modulus 171 GPa, Poison's ratio 0.28 [22] and abrasive size 50 nm were used in the calculation). This is the key abrasive loading condition to mechanically remove the material without residual damage in polished silicon.

In summary, this study has explored the possibility and mechanism of damage-free polishing of monocrystalline silicon by a mechanical process without chemical additives. It concludes that depending on the abrasive size and nominal pressure applied, all types of damages reported in the literature can be eliminated by avoiding the initiation of β-tin.

The authors thank the Australian Research Council for continuing support of this project. AQB is financially supported by the University of Sydney's IRS scholarship.

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