Surface Damage Effects in Ultrasonic Cleaning of Silicon Wafers

A. Nadtochiy[1], A. Podolian[1], O. Korotchenkov[1], D. Kalinichenko[1], L. Steblenko[1], J. Schmid[2], E. Kancsar[2], V. Schlosser[2]
[1] Kyiv National University, Kyiv 01601, Ukraine;
[2] University of Vienna, A-1090 Wien, Austria;

Abstract

The cleaning of Si wafers due to kHz-frequency ultrasonic treatment in a water-containing bath is studied. The cleaning stages observed with varying treatment time are discussed. It is found that, during the first 60-90 min, organic hydrocarbon contaminants can be effectively removed from the wafer surface. This is evidenced by the disappearance of organic-related absorption peaks and remarkable shortening of the photovoltage decay transients. At longer times, the subsurface crystalline quality is degraded and the wafer performance gradually deteriorates. The decay curves become double-exponential profiles, developing fast initial decays and longer ones at greater instants, indicative of a subsurface trap generation at this treatment stage. This is accompanied by the broadening of the X-ray rocking curves. The likely origin of the presented effects is discussed.

Introduction

Cleaning of surfaces in silicon wafers has become one of the most critical operations in device processing technologies. The complete removal of contaminations and the passivation of rechargeable states on the surfaces are very important issues for improving energy conversion efficiency of Si solar cells.

Ultrasonic treatment (UST) is a promising tool to clean Si wafers with the benefit of reducing hazardous waste [1, 2]. Since the force imparted by acoustic cavitation and streaming is non-selective, not only contaminants but also wafers can be attacked. It is assumed that a damage threshold for UST energy exists, although the physical mechanism behind the ultrasonic-induced damage is not completely understood.

Here, we study an interplay of the surface cleaning and damage effects of Si wafers subjected to a kHz-frequency UST, which is performed in distilled water.

Experimental

Samples of *n*-Si (P doped to 4.5 Ohm·cm resistivity, 460-μm thickness) from (111)-oriented, Cz-pulled wafers are used. The density of misfit dislocations is $\sim 10^2$ cm^{-2} The sample surface was initially degreased with acetone, and then covered with a thin layer of vaseline (soft paraffin), consisting of chained hydrocarbons and mimicking a hydrocarbon contaminant on Si wafers [3]. The acoustic power delivered at the Si-liquid interface is fixed at about 10 W/cm^2 at a bath temperature of 60-70°C.

Several surface sensitive techniques, including surface photovoltage (SPV) decay transients and optical transmission spectra, are used to trace the removal of particulate and organic contaminants. SPV transients were measured using a 406 nm LED pump pulse in the contactless capacitor arrangement. Fourier transformed-infrared (FTIR) spectra were obtained using a JASCO 5300 spectrometer.

Double-crystal X-ray diffraction measurements [4] were used in order to trace the strain status of the subsurface region and to study the damage effects of UST. High-resolution x-ray rocking curves (XRC) were performed using Cu Kα_1 radiation.

Results and Discussion

Removal of the organic contaminants from the wafer surfaces was studied observing organic-related FTIR absorption peaks and SPV decay transients. Figure 1

shows typical absorption spectra taken in the C–H stretch vibration region for the Si wafer surface before (spectrum 1) and after (2) UST. Two peaks are clearly resolved in spectrum 1 at 2850 and 2920 cm^{-1}, which are close to the C–H stretch vibrations of groups $-CH_3$ and $-CH_2$-, and of $-CH_2$-, respectively [5]. It is found that, applying UST during the first 40-90 min (referred to as stage 1), the organic contaminant is effectively removed from the wafer surface. This is supported by the fact that the FTIR absorption peaks disappear in spectrum 2 of Fig. 1.

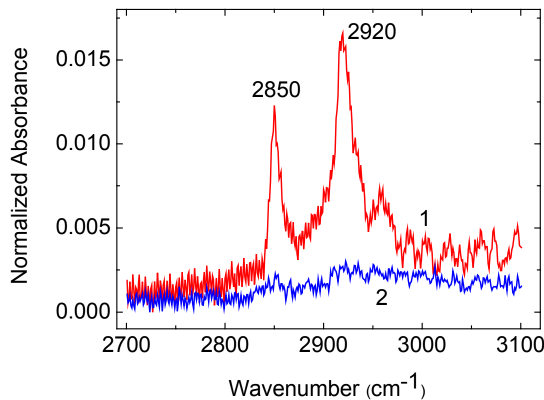

Fig. 1. FTIR spectra of a Si wafer covered with a thin layer of vaseline taken before (1) and at the first stage of UST (2).

This conclusion is also supported by remarkable shortening of the SPV decay transients (curve 2 in Fig. 2 compared with curve 1). Indeed, the minority carrier lifetimes (τ) deduced from the decays are effective lifetimes integrating bulk (τ_b) and surface (τ_s) recombination components. The shortening of the observed SPV decay indicates a reduced τ_s caused by surface reactions during UST, which could be a creation of dangling bonds on the bare Si surface due to a local removal of SiO_2 by cavitating bubbles.

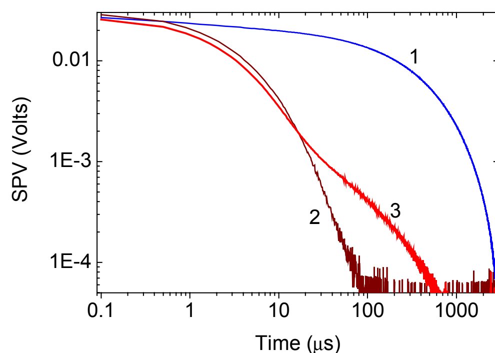

Fig. 2. SPV decays of a Si wafer taken before (curve 1) and after UST at stages 1 (2) and 2 (3).

At longer UST times (stage 2, performed during 90-150 min), the wafer performance gradually deteriorates. Thus, the decay curves become double-exponential profiles, developing fast initial decays (cf. at time instants less than 10-20 μs in curve 3 of Fig. 2) and revealing longer ones at greater instants (>20 μs in curve 3). This fact can be interpreted by two mechanism caused by the presence of traps and recombination centers. The initial decays ($t<10\mu s$), when the injected carrier concentration is large compared with the density of the trapping centers N_t, are governed by the time constant of the recombination centers. Once the injected carrier concentration becomes small compared with N_t ($t>20\mu s$), the decay again is simple exponential determined by N_t. Of importance is the fact that the initial decays observed at ≤10 μs in curves 2 and 3 are nearly identical, indicative of a clean wafer

surface. Therefore, a subsurface trap generation, referred to as subsurface damage, is stimulated by elongated exposure to UST (greater than 60-90 min).

This assumption is confirmed by the broadening of the X-ray rocking curve observed for stage 2 (curve 3 in Fig. 3) of the UST. XRCs are broadened when defects are present. At short UST exposures (curve 2 compared with 1 in Fig. 3) the XRC becomes narrower compared to to the initial result (curves 2 and 1 in Fig. 3). Therefore, the subsurface crystalline quality deduced from XRC full width half maximum (FWHM) is degraded at stage 2, which is accompanied by an enhanced trap concentration observed in the SPV experiments. A likely explaination is the increase of the subsurface impurity concentration caused e.g. by oxygen. Although the exact nature of the defect redistributions behind the observed XRC broadening is unexplored, it would be reasonable to assume that oxygen precipitation would occur due to enhanced oxygen diffusion caused by the presence of local strain fields and elevated temperatures inside a cavitating bubble striking the Si surface. Of further significance may be hydrogen molecules decomposed in water and subsequently trapped at the silicon surface. This can explain the shortening of the SPV decays observed in curves 2 and 3 of Fig. 2, although it is unlikely that hydrogen itself can produce enough strain to explain the SRC broadening. Meanwhile, it can decorate the dislocation cores thus modifying the dislocation strain fields and introducing into the varying XRC FWHM.

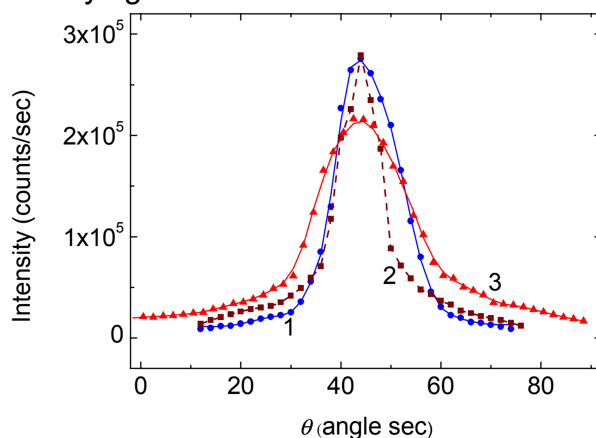

Fig. 3. X-ray rocking curve measurements performed near the (111) diffraction pattern at 14° 13′′ on a Si wafer before (curve 1) and after UST at stages 1 (2) and 2 (3). Full widths at half maxima are 14.6 (curve 1), 10.3 (2) and 20.4 (3) sec.

Conclusions

Two stages of the Si wafer cleaning in the water-containing ultrasonic bath are observed. During the first 60-90 min, organic hydrocarbon contaminants are effectively removed from the wafer surface. Exposing wafers to UST longer however degrades the crystalline subsurface quality and the wafer performance gradually deteriorates. Our results can contribute to the optimized development of an environmental friendly cleaning steps in Si wafer preparation.

Acknowledgement

This work was supported by the Austrian-Ukrainian Cooperative Agreement No. UA 09/2009 (Mitteln des Bundesministeriums für Wissenschaft und Forschung / Die Österreichische Austauschdienst-GmbH) and No. M/110-2009 (Ministry of Education and Science of Ukraine).

References

[1] G. W. Gale and A. A. Busnaina, Particulate Sci. Technol. **13** 197 (1995).
[2] M. Keswani, S. Raghavan, P. Deymier, and S. Verhaverbeke, Microelectron. Eng. **86** 132 (2009).
[3] K. Saga and T. Hattori, J. Electrochem. Soc. **143** 3279 (1996).
[4] A. Iberl, H. Göbel and H. Heinecke, J. Phys. D: Appl. Phys. **28** (1995) A172.
[5] M. Endo, H. Yoshida, Y. Maeda, N. Miyamoto, and M. Niwano, Appl. Phys. Lett. **75** 519 (1999).