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Doping of silicon by carbon during laser ablation process

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Abstract. Effect of laser ablation on properties of remaining material was investigated in silicon. It was established that laser cutting of wafers in air induced doping of silicon by carbon. The effect was found to be more distinct by the use of higher laser power or UV radiation. Carbon ions created bonds with silicon in the depth of silicon. Formation of the silicon carbide type bonds was confirmed by SIMS, XPS and AES measurements. Modeling of the carbon diffusion was performed to clarify its depth profile in silicon. Photo-chemical reactions of such type changed the structure of material and could be a reason for the reduced quality of machining. A controlled atmosphere was applied to prevent carbonization of silicon during laser cutting.

1. Introduction

Laser ablation is widely used in analytic sampling [1], deposition [2] and laser micro-fabrication [3]. Ablation is a key process for many laser applications. Laser cutting and scribing of silicon wafers are widely used in semiconductor industry. Here, numerous laser pulses are required to ablate an appreciable amount of material. The quality of such processing in almost all cases is typically evaluated by geometric shape of the excisions together with the formation or absence of mechanical defects such as cracks. Structural modification has been used to determine the depth of the affected layer [4]. However, investigations of chemical changes in elemental material such as silicon were not properly addressed.

Laser radiation is typically absorbed in a thin surface layer of the material within the thickness of α^{-1} , where α is the absorption coefficient at the laser wavelength. Even with ultra-short pulses, a significant part of the laser energy is deposited into the substrate as heat [5]. Thermal conductivity is responsible for dissipation of the excess energy. Evaporation of material leads to ignition of plasma by laser beam in a few picoseconds. The temperature in laser ablation plasma reaches 10^3-10^4 K [6]. Being in close thermal contact with the substrate, the plasma also acts as an ablating tool. Further, the plasma actively reacts with the ambient air creating ions that can be adsorbed onto the surface. Therefore, the surface features formed in air are likely to be influenced by such ablation products as well as by dopants that become mobile during the high temperature laser heating cycle [7].

Ablation of silicon with short pulse lasers was investigated in various processing regimes. The laser cut edges formed during the processing were analyzed. It was established that laser cutting of wafers in air initiated doping of the silicon by carbon. This effect was most pronounced at higher laser power or by using UV radiation. Carbon ions formed chemical bonds with silicon within the bulk substrate. Formation of silicon carbide was confirmed by surface spectroscopy. Conversely, a shielding atmosphere was found to prevent carbonization of silicon surface during laser ablation.

2. Sample preparation and experimental

Silicon wafers (p-Si {111}) with the thickness of 550 µm were irradiated with lasers of various pulse durations of 60 ps (PL2241, Ekspla) and 130 fs (Superspitfire, Spectra Physics) using the experimental

set-up described in detail in [8]. The range for "gentle" ablation of silicon with a picosecond laser had been defined and all the experiments in this work were performed below the limit of crack formation. The cutting was performed by multiple passes along a cutting line. The pulse energy and pulse overlap as well as the number of passes were varied. For experiments in the controlled atmosphere, the samples were placed inside a vacuum chamber having a fused silica window. Rough vacuum was created by a rotary pump and the chamber was later filled with nitrogen (99.95 %).

In order to varying the layer thickness disturbed by laser cutting, a set of samples were laser exposed with various pulse durations, wavelengths and power as presented in table 1. A silicon wafer was cleaved, but not laser treated to provide a fresh reference sample.

Table 1. Laser exposure conditions of Si				
prepared for surface analysis.				
#	sample	laser		
		λ, nm	τ, ps	F, J/cm ²
1	UV ps-cut in air	266	60	16
2	ps-cut in air	1064	60	42
3	ps-cut in air	1064	60	84
4	ps-cut in air	1064	60	125
5	ps-cut in vacuum	1064	60	84
6	ps-cut in nitrogen	1064	60	84
7	fs-cut in air	800	0,13	57
8	fresh cleaved surface			
9	thermally oxidized Si			



Figure 1. SEM images of the original wall cut by the laser in the area of the channel formation (left) and a crater etched with the ion beam in the same area (right).

Chemical composition and the chemical bonding of the laser cut edge was characterized by X-ray photoelectron spectroscopy (XPS) (Riber, model LAS-3000). The fine structure of XPS spectral lines was analyzed with *XPSPEAK41* software. As a reference, the *-CH* peak of the *C 1s* spectrum (284.6 eV) was used. A focused beam of Ar-ions (7 keV) was used for secondary ion mass-spectroscopy (SIMS) experiments, following cleaning of surfaces, loading into the vacuum chamber and etching of the depth profile. The ion beam dimension for etching was 0.3 x 0.3 mm². Only the central part (10%) of an etch crater was used for the mass spectroscopy analysis. Auger-electrons were excited by the electron beam (3 keV) with a spatial resolution of 2.5 μ m. The elemental profile was measured on a fresh cleavage made in air and cleaned by Ar-ions in vacuum.

3. Results

3.1. Laser processing

Laser cutting in air generated deposits around the ablation area. For cutting in nitrogen ambient, a much larger quantity of deposits were made that looked like sand. In vacuum only little deposition was observed together with a coloration of the wafer surface. The surface was oxidized by the higher temperatures that result from reduced thermal dissipation in vacuum. The cutting speed of the wafer was the highest in vacuum, while it was about two times slower in nitrogen. UV radiation at 266 nm drove faster wafer penetration compared to IR radiation of nano- and femtosecond lasers applied at the same fluence. On the other hand, the volumetric ablation rate for the femtosecond laser with similar fluence was larger leading to higher cutting speed.

The quality of ablation edges was good on the wafer entry side. However, starting from a depth of about 100 μ m, channels were formed that penetrated through the wafer every 30-50 μ m, especially when processing with the UV picosecond laser. Similar results were observed with femtosecond [9] and nanosecond lasers [10]. A close view of the cutting edge in the area of channeling (left) is shown in figure 1 together with a laser-formed edge in the same area (right) sectioned by ion-beam milling during SIMS. The edged structure created during laser ablation (channels) disappeared after ion-beam etching and transformed into a bubble-like structure with grains. The depth of the etched crater is 20 μ m.

3.2. X-ray electron spectroscopy (XPS)

Fine structure analysis and deconvolution of the XPS spectral peaks enabled quantitative assessment of chemical structure changes induced by the laser irradiation. The main component of the *Si* 2p line located at 103.2 eV (figure 2) was in agreement with the position of the SiO_2 peak in thermally oxidized silicon (sample #9). The position of the low energy peak (98 eV) was in agreement with neutral state of a silicon atom [11]. Between these two energies, additional components corresponding to intermediate ionization states of silicon were observed in all samples cut by laser in air independent of pulse duration and wavelength. These components are assigned to *Si-C* bonds (100.45 eV) and pseudomorphous configurations of silicon oxi-carbide *Si-O-C* (102.1 eV) [12]. Since a thinner oxide layer was formed during laser cutting at low-power, Si⁰ lines were seen only in these samples after prolonged ion milling (10 min.). UV radiation of 266 nm created a thick oxide layers even at lower power and could not be removed after 10 min. of etching. The relative intensity of the SiC component increased after etching (figure 2). This is evidence that small carbon atoms penetrated deep into the sample during laser processing even in the presence of ambient oxygen.





Figure 2. Normalized XPS spectra of Si 2p line in samples #2 (1), #3 (2), #4 (3) cut with the 1064 nm ps-laser and ion-etched for 10 min, and in reference sample #9 (4). Fitted spectral structures in #3 (1): 1a - 98 eV (Si⁰); 1b - 100.45 eV (Si-C); 1c - 102.1 eV (Si-O-C); 1d - 103.2 eV (SiO₂); 1e - 104.7 eV.

Figure 3. Normalized XPS spectra of C 1s line in samples #2 (1, 2) and #3 (3, 4) cut with the 1064 nm laser: "as-cut"(1, 3) and after ion-etching for 10 min. (2, 4). Positions of lines related to -CH and Si-C bonds are shown.

Residual gases in the chamber together with poor heat dissipation by the reduced pressure led to creation of an oxide film during laser ablation in vacuum. *Si-N* bonds were detected in sample #6, laser cut in nitrogen. Although the *Si-N Si 2p* line at about 102 eV overlaps with the *Si-C* line, the latter was discounted because SiC ions were not observed in SIMS analysis of the same sample. Elemental silicon (Si⁰) was also clearly detected in sample #6.

The carbon *C* 1s line of laser cut samples remained in the XPS spectra after ion-beam etching, while adsorbed hydrocarbon disappeared shortly as ion-milling cut through the thermally oxidized silicon surface. Similar trends are noted for the *C* 1s line of sample #2, as evidenced by the transformation of the central peak associated with -*CH* bond after ion etching (figure 3) into double peaks where the low energy peak at 282.4 eV is associated with the *C*-Si bond. The other *C* 1s peak at about 286.3 eV is a typical characteristic of oxidized carbon species, in particular carbonyl species of the types CO [13], or could also be associated with the *Si*-*O*-*C* bond [14].

3.3. Secondary ion mass-spectroscopy (SIMS)

SIMS spectra of all the samples were measured immediately after laser machining and again after ionbeam etching for 5-10 min. Different combinations of Si, O, C content and, in some samples, of N ions were detected. The ion-etching rate was 4 times slower in the area of "channel" formation as compared to the upper part of the channel edge. The relative intensity of the lines were changed by the laser processing conditions, yielding different depth profiles of atomic species. Even with femtosecond laser cutting, a disordered layer of 2 μ m thickness was found. Ion-depth profiling showed that elemental carbon disappeared quicker than its combination in SiC, which was incorporated below the surface. The distribution of silicon sub-oxides was stipulated by the depth profile of oxygen.

3.4. Auger electron spectroscopy (AES)

Fresh cleavage of the wafer perpendicularly to the laser cutting line was used for AES analysis. The cleaved surface was cleaned by Ar-ions after placement in vacuum. Electron beam scans were made on the cleaved surface along tracks (#1,2,3, and 4 in inset in figure 4) offset from the laser-cut channel to provide the depth-profile carbon concentrations shown in figure 4. Residual contamination of adsorbed hydrocarbons caused the background carbon reading far from the laser processed surface. The accuracy of atomic concentration was ~10%.

The carbon concentration obtained in parallel with the laser-cut surface (line #1) showed nonmonotonous behaviour of the C impurities through the depth of the silicon wafer. Areas nearest to the laser formed channels (lines #1,2) yielded the highest concentration of carbon. Deep lateral penetration of carbon was observed up to 25 μ m from the laser-cut surface (lines #2,3) into the bulk of material.



laser entry side laser cut surface Si wafer

Figure 4. Depth-profile distribution (left) of C atoms in silicon wafer sample #4 measured by AES on freshly cleaved surface in bisecting the laser-cut edge (see arrows in insert above): 1- uncleaned surface after incorporation into a vacuum chamber, near the cut; $2 - 15 \ \mu m$ off the edge; 3- 30 $\ \mu m$ off the edge; 4- far away from the edge.

4. Discussion

Laser cutting of silicon wafers by multiple scans with overlapping laser pulses is a cyclic process. The cycle includes drastic temperature variation with periods of time long enough for adsorption of hydrocarbons and other gases. Hydrocarbon molecules are always present in the air as pollutants and have good ability to be adsorbed on surfaces. An equilibrium solubility of carbon substitutionally dissolved in Si is 10^{18} cm⁻³ at 1300° C [7]. Solubility of interstitial carbon is less by more orders of magnitude. However, such hydrocarbons could not cause a high level of doping at the depth of a few micrometers. It is more likely that the source of doping is the reaction with CO₂ gas, one main atmospheric component. CO₂ molecules could be caught on the boiling front in the form of bubbles. Even at later dissolution in silicon, the CO₂ molecules remained in the bulk due to their large size. Complexes corresponding to CO and CO₂ molecules may be fast diffusing entities in silicon [7].

The laser-interaction volume at the ablation front remains near the melting point for a long time of up to 1 μ s [6] after every laser pulse. The effective time for high-temperature thermal diffusion increases by periodical laser scanning to as long as 1-2 ms for complete cutting of the wafer. During this time, the diffusion length of interstitial carbon near melting temperature (1685 K) is at least 4-5 μ m, the distance comparable with depth of incorporated carbon from AES characterization.

Laser ablation and plasma created inside the kerf heat the surrounding silicon material well above 1193 K, the temperature of silicon carbide formation defined in thin film experiments [15]. Stoichiometric SiC is the only stable compound permitted by the Si-C phase diagram. Carbon atoms adsorbed on top of the silicon surface move very easily from the surface into sub-surface substitutional sites. On the contrary, the *Si-N* bonds undergo oxidation at high temperatures and are completely replaced by *Si-O* bonds above 1273 K [16]. Therefore, no nitrogen was detected in the samples prepared in the presence of oxygen. Depth profiles from the SIMS spectra show that silicon-carbon complexes (SiC) are located under the surface. The presence of silicon carbide type bounds on the laser-cut surface was also confirmed by high-resolution XPS spectra (figures 2 and 3).

For UV laser irradiation, the high temperature plasma was able to dissociate molecules and produce ions that actively create bonds with silicon. Grains of silicon carbide were able to change reflective properties of the surface formed by the laser, leading to "channel" formation. The chemistry of the possible laser-induced processes requires further investigation.

5. Conclusion

The interaction of silicon surfaces with air molecules during laser ablation together with the laserradiation and laser-ignited plasma processes are responsible for several thermo-chemical reactions. Thermal gradients are sent to drive diffusion of surface-adsorbed ions, leading to doping of silicon by carbon. Silicon carbide type bonds were formed below the surface and could be the reason for the "channeling" observed during wafer cutting. Shielding gas of nitrogen can prevent carbonization of the surface.

Acknowledgments

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References

- [1] Bogaerts A, Chen Z, Gijbels R and Vertes A 2003 Spectrochimica Acta B 58 1867
- [2] Chrisey D B, Pique A, McGill R A, Horwitz J S, Ringeisen B R, Bubb D M and Wu P K 2003 *Chem. Rev.* **103** 553
- [3] Meijer J, Du K, Gillner A, Hoffmann D, Kovalenko V S, Masuzawa T, Ostendorf A, Poprawe R and Schul W 2002 *CIRP annals STC E* **50** 531-550, ISBN 1726-0604
- [4] Luft A, Franz U, Emsermann A. and Kaspar J. 1996 Appl. Phys. A 63 93-101
- [5] Ohmura E, Fukumoto I and Miyamoto I 2002, Proc. of SPIE, 4830 462-6
- [6] Femtosecond Technology for Technical and Medical Applications 2004 *Topics in Applied Physics*, **96** eds Dausinger F, Lichtner F and Lubatschowski H 326 ISBN: 3-540-20114-9
- [7] Goesele U, Laveant P, Scholz R, Engler N and Werner P 2000 Materials Research Society Symposium Proc. 610 B7.1-12
- [8] Raciukaitis G, Jacinavicius S, Brikas M and Balickas S 2003 Proc. of the 22nd Int. Congress on Applications of Lasers & Electro-Optics ICALEO 2003, (Jacksonville, USA, 2003) 134-41
- [9] Ostendorf A, Kulik C and Baersch N 2003 Proc. of the 22nd Int. Congress on Applications of Lasers & Electro-Optics ICALEO 2003, (Jacksonville, USA, 2003) 20-28
- [10] Corboline T, Rea E C and Dunskey C 2003 Proc. of SPIE **5063** 495-500
- [11] Fundamental XPS data from pure elements, pure oxides, and chemical compounds 1999 XPS International Inc.
- [12] Avila A, Montero I, Galan L, Ripalda J M and Levy R 2000 J.Appl. Phys. 89 212-6
- [13] Benndorf C, Caus C, Egert B, Seidel H and Theime F 1980 J. Electron. Spectrosc. Relat. Phenom. 19 77
- [14] Tan Y S, Chooi S Y M, Sin C Y, Ee P Y, Srinivasan M P and Pehkonen S O 2004 Thin Solid Films 462-463 250-256
- [15] Osten H J, Methfessel M, Lippert G and Rucker H 1995 Phys. Rev. B. 52 12179-83
- [16] Tokuse M, Oyama R, Nakagawa H and Nakabayashi I 2001 Analytical Sciences 17 281-4