

Excimer laser-assisted chemical process for formation of hydrophobic surface of Si (001)

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Abstract Silicon (Si) wettability is one of the important parameters in the development of Si-based biosensing and lab-on-chip devices. We report on UV laser induced hydrophobicity of Si (001) wafers immersed in methanol during the irradiation with an ArF excimer laser. The irradiation with 800 pulses of the laser operating at 65 mJ/cm² allowed to significantly increase the hydrophobicity of investigated samples as characterized by the static contact angle change from 77° to 103°. Owing to the irradiation with relatively low laser fluence, no measurable change in surface morphology of the irradiated samples has been observed with atomic force microscopy measurements. The nature of the hydrophobic surface of investigated samples is consistent with X-ray photoelectron spectroscopy analysis that indicates formation of Si–O–CH₃ bonds on the surface of the laser-irradiated material.

1 Introduction

Selective area control of Si wettability and, in particular, fabrication of surfaces with wettability gradients has received significant attention due to the growing applications of this material in microfluidic and lab-on-chip device areas [1, 2]. Reduced wettability is often obtained by both increasing surface roughness and surface chemical modification [3]. The surface roughening techniques to produce

disordered/ordered surface structures on Si include photolithography [4], ion-beam lithography [5] and direct laser structuring [6]. Laser structuring of surfaces is a relatively simple process with the potential to offer nanostructuring with high spatial resolution [7]. Femtosecond laser has been reported to generate nanostructures on the Si surface and induce a superhydrophobic surface with a contact angle (CA) exceeding 150° [8]. However, as Si has a high laser texturing threshold (~ 500 mJ/cm²) [9], surface nanostructuring always requires a relatively high power laser irradiation, frequently carried out in an atmosphere of reactive gasses [3, 6, 7]. To avoid this complication, numerous experiments have been focused on laser-induced/-assisted surface chemical modification, involving deposition of organic/metal oxide films on the Si substrate before irradiation [10, 11]. It is known that a chemically induced hydrophilicity of Si is due to formation of a singular and associated –OH groups on the surface, while a hydrophobicity is mainly due to the presence of Si–H and/or Si–(O)–CH_x groups [12]. To achieve selective area control of wettability of Si, complex patterning steps are usually required, including treatment in chemical solutions [13]. High chemical reactivity of UV laser radiation has also been used to selective area process organic film coated solid substrates and modify their hydrophobicity [11]. However, a limited amount of data is available on laser-assisted modification of Si wettability by irradiation of samples immersed in different chemical solutions. It has been reported that a 1 % HF treated Si surface immersed in methanol (CH₃OH) solution for 20 min becomes coated with –OCH₃ through the reaction with Si dangling bonds [14]. Furthermore, the CH₃OH vapor is known to have a strong absorption band in the 105–200 nm region, and it can be dissociated relatively easily with 157 and 193 nm lasers to form H atoms and –OCH₃ radicals [15–17].

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In our previous work, a UV laser was used to modify the chemical composition of InP surfaces exposed to air, SiO₂ or deionized water environments [18–20]. In this paper, we expand this approach on studying laser-assisted modification of surface chemistry of Si (001) samples immersed in CH₃OH, aiming for the formation of a strongly hydrophobic material.

2 Experimental

A series of 12 mm × 6 mm samples were selected from 380 μm thick P-doped (n-type) (100) Si wafer with a resistivity of 3.1–4.8 Ω m (SVM Inc.). The samples were first cleaned by Opticlear, acetone and isopropyl alcohol, each for 5 min, then were lightly etched by a diluted 1:50 HF (48 %) (Anachemia Science) solution for 1 min to remove the native oxides [14] and, finally, rinsed with DI water and dried with nitrogen (N₂). The samples were immersed into a 0.74-mm tall microfluidic chamber filled with a degassed methanol solution. The chamber was capped with a UV transparent (transmission >90 %) fused silica window, and designed to provide a continuous injection of methanol above the sample surface during irradiation. The irradiation was carried out with ArF (λ = 193 nm) and KrF (λ = 248 nm) excimer laser (Lumonics, Pulse Master 800)-based systems described elsewhere [18, 21]. The homogenized beam was used to project a mask that produced circular spots on the sample surface at demagnification ratios of 2.6 and 1.8 for the ArF and KrF setups, respectively. With a computer controlled positioning, the setups allow in processing of the same sample at numerous sites. Following irradiation, samples were rinsed with DI water, dried with N₂ and installed in a sealed N₂ container designed to eliminate their exposure to an atmospheric environment, and transported for further surface characterization.

Static CA measurements were carried out using a goniometer (Rame-Hart NRL, Model 100) operating at room temperature and ambient humidity. Water drops, approximately 5 μL in volume, were produced from high-purity deionized water of electrical resistivity typically 17.95 MΩ cm. The volume of each drop was relatively small, so the gravitation forces played a negligible role in its deformation. Furthermore, because the volume of a drop used in each test was nominally the same, the error originating from its potential deformation was comparable, thus, not affecting our conclusions. The profile images of the sessile water drop, on the samples were captured by a CCD camera (Logitech). Four different and independent measurements were performed on the sites irradiated under the same conditions. Drop image was processed by VP-eye

6.0 software (MMedia) and the CA value was determined by drop analysis pluggins of ImageJ software.

Excimer laser processed surfaces were analysed with a Kratos Analytical, AXIS Ultra DLD X-ray photoelectron spectrometer (XPS) operating at a take-off angle (TOF) of 60°. The XPS analysis was carried out following the procedure described elsewhere [20].

Sample surface morphology was imaged with a Digital Instrument, Nanoscope III AFM operating in a tapping mode over the 5 μm × 5 μm region, which allowed for a high accurate roughness analysis and surface morphology imaging [21].

3 Results and discussion

3.1 Contact angle measurements

Figure 1 shows the CA values measured for Si (001) samples that were immersed in methanol and irradiated with the ArF laser at pulse fluence of 30, 65 and 80 mJ/cm². It can be seen that CA of the sites irradiated with 800 pulses at 65 mJ/cm² increases from its initial value of 77° to 103°. A comparable result is observed for the 1,000-pulse irradiated sites. This suggests that the laser induced CA modification of the Si surface saturates for the applied laser fluence. A more intense dynamic of the CA increase has been observed for 80 mJ/cm² and low number of laser pulses ($N < 200$), as indicated by the full circle symbols in Fig. 1. However, the formation of bubbles on the samples

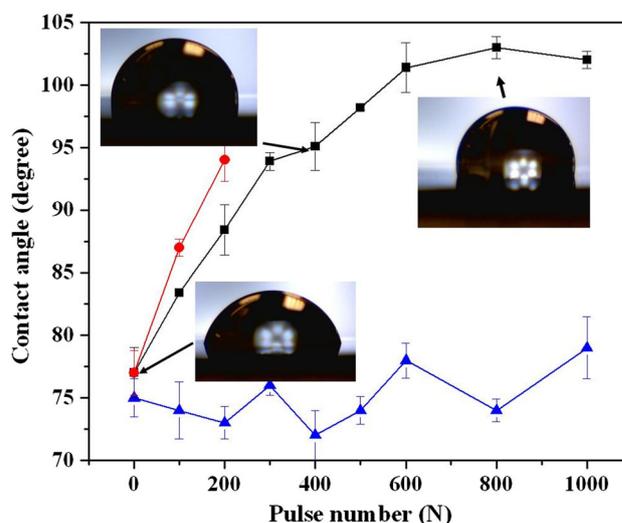


Fig. 1 Contact angle of Si (001) samples immersed in methanol and irradiated with an ArF laser at 30 mJ/cm² (filled triangle), 65 mJ/cm² (filled square) and 80 mJ/cm² (filled circle). The error bars are calculated based on the measurements of four independent sites

irradiated with $N > 200$ pulses, and a related uncontrolled modification of the sample surface morphology prevented us from collecting reliable data under such conditions. Using an approach described elsewhere [20, 22], we estimated that a 65 mJ/cm^2 pulse of the ArF laser induces peak temperature on the Si surface comparable to the methanol boiling point, i.e., 65°C [23]. Thus, the irradiation with greater laser fluence leads to the formation of a large amount of bubbles. We have observed that, indeed, the surface concentration of bubbles increased in this case drastically, in proportion to the number of laser pulses delivered to the surface. Consistent with this was our inability to fabricate Si samples of satisfactory characteristics with the laser fluence of 80 mJ/cm^2 and $N > 200$ pulses. In contrast, the irradiation of 30 mJ/cm^2 showed only a weak increase of CA to 78° for the 1,000-pulse irradiated sites.

Experiments involving KrF laser revealed no significant change of CA for samples irradiated up to 182 mJ/cm^2 . The irradiation with fluence of 250 mJ/cm^2 resulted in an intensive formation of bubbles, consistent with the ability of an individual pulse of such a fluence to increase the temperature of the Si wafer (immersed in methanol) to the boiling point of methanol. No measurable increase of CA could be recorded for samples irradiated under these conditions with up to 1,000 pulses. A negative response of Si

to KrF laser-induced chemical modification of its surface in methanol seems to be related to the inability of this laser to photodissociate CH_3OH and create $-\text{OCH}_3$ radicals required in the formation of a hydrophobic surface [15, 17].

The CA values of the ArF laser irradiated samples remained unchanged for up to 4 h if the samples were stored in N_2 . However, following a 20-h storage in air environment, we observed CA decreased to 56° , which is likely related to the oxidation of Si and formation of SiO_2 on its surface [24]. Note that CA ~ 50 to 65° has been reported for Si samples passivated with naturally grown SiO_2 [25].

3.2 AFM analysis

Figure 2 shows AFM images of a non-irradiated Si sample that was etched with HF and rinsed with DI water, and a sample (site) immersed in methanol and irradiated with 500 pulses with ArF laser at 65 mJ/cm^2 . The AFM roughness (σ_{RMS}) measured for the 500 pulse irradiated site is 0.37 nm , which is comparable to $\sigma_{\text{RMS}} = 0.31 \text{ nm}$ for the non-irradiated sample. Clearly, no obvious laser induced surface morphology modification could be indentified with the AFM measurements. Thus, the hydrophobic nature of the material irradiated in methanol must be related to the laser induced chemical modification of its surface.

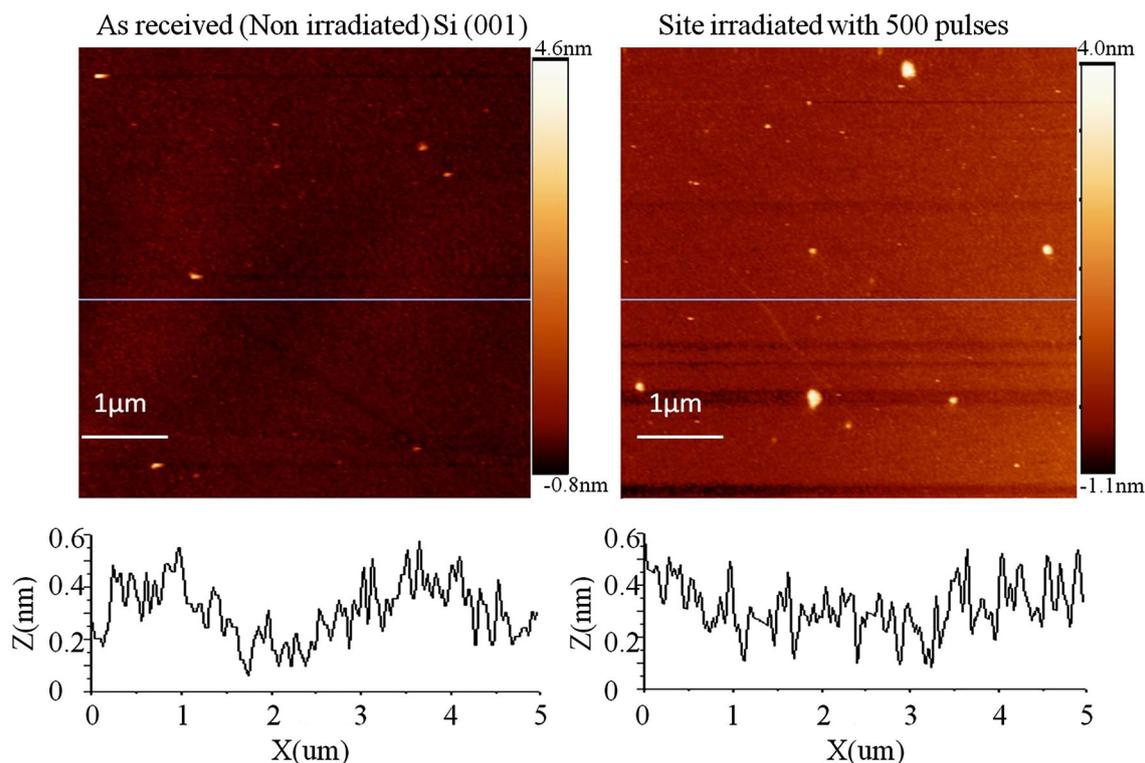


Fig. 2 AFM image of a non-irradiated Si (001) sample and a site irradiated with 500 pulses by an ArF laser operating at 65 mJ/cm^2

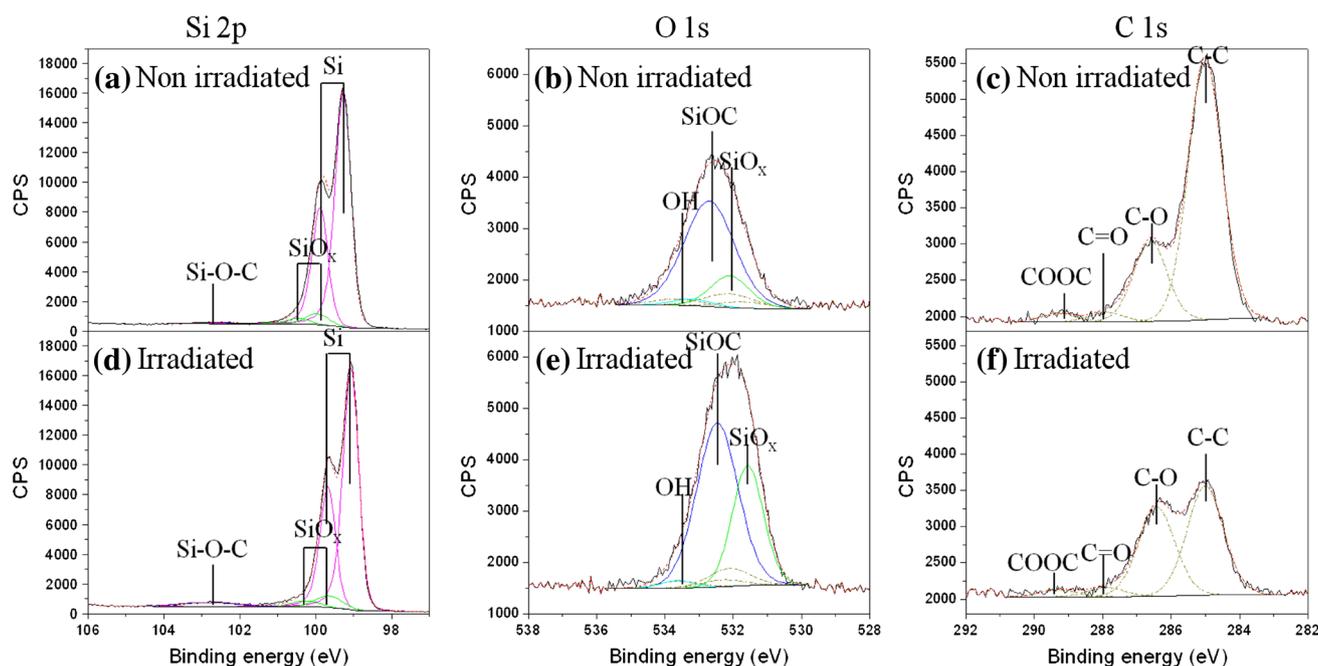


Fig. 3 XPS Si 2p, O 1s and C 1s spectra of a reference (non-irradiated) sample (a–c), and a sample immersed in methanol and irradiated with 500 pulses of an ArF laser at 65 mJ/cm^2 (d–f)

3.3 XPS analysis

Figure 3 shows XPS spectra of Si 2p, O 1s and C 1s for a non-irradiated sample (a–c), and a sample immersed in methanol and irradiated with 500 pulses of the ArF laser at 65 mJ/cm^2 (d–f). A weak feature, indicated as Si–O–C in the Si 2p spectrum of the non-irradiated site (Fig. 3a) can be seen around $\text{BE} = 102.7 \text{ eV}$. This feature has been reported to originate from the $\text{Si}-(\text{OCH}_3)_x$ bond [26]. The atomic concentration of this compound was estimated at 0.7 %, which probably is slightly underestimated due to the relatively small (60°) TOF applied while collecting our XPS data [12, 14]. On the irradiated site shown in Fig. 3d, the atomic concentration of $\text{Si}-(\text{OCH}_3)_x$ has been estimated at 3.5 %, which indicates a significant 5-fold increase of the surface concentration of this compound. In the O 1s spectra (Fig. 3b, e), the $\text{Si}-(\text{OCH}_3)_x$ peak ($\text{BE} = 532.6 \text{ eV}$) increases from 1 % for the non-irradiated material to 2.5 % for the irradiated site. In the C 1s spectra (Fig. 3c, f), the C–O bond from original C absorbates overlaps with $\text{Si}-(\text{OCH}_3)_x$, so the C–O increment ratio is not as significant as in the Si 2p and O 1s spectra. As $\text{Si}-(\text{OCH}_3)_x$ is responsible for the hydrophobic nature of the Si surface [12, 27, 28], the increase of the surface concentration of this compound appears to be the main reason for the observed enhancement of the hydrophobic characteristics of the ArF laser irradiated Si samples. With increasing laser fluence, more $-\text{OCH}_3$ is expected to be created and absorbed on the Si surface [29]. The saturation of CA around 103° is related to

the CH_3 surface energy. The lower the surface energy, the higher the hydrophobicity is expected. It has been reported that the closest hexagonal packing of $-\text{CF}_3$ groups gives the lowest surface free energy of any solid, with CA of near 120° [30].

In the O 1s spectra, besides Si–O–C and C–O, there are also SiO_x and OH related peaks. The increase of the SiO_x peak is possibly due to the OCH_3 bond to the sub-oxides ($\text{SiO}_{x+1}-\text{CH}_3$) [26]. As the HF treated Si sample didn't show the presence of OH (not shown here), the OH peak is possibly due to CH_3OH physically absorbed on the surface.

XPS study of the samples irradiated in methanol with up to 500 pulses of the KrF laser at 250 mJ/cm^2 showed no evidence of the increased surface concentration of Si–O–C. This result is consistent with the inability of the KrF laser, in contrast to the ArF laser, to photodissociate methanol and create $-\text{OCH}_3$ radicals [15, 16].

4 Conclusion

The mechanism of laser-induced wettability of Si surface has been investigated by irradiation of samples immersed in methanol using ArF and KrF excimer lasers. The formation of Si (001) hydrophobic surface with CA of 103° (an increase from the initial CA of 77°) has been observed for irradiation with 800–1,000 pulses of the ArF laser at 65 mJ/cm^2 . XPS results suggest laser-induced formation of $\text{Si}-(\text{OCH}_3)_x$ compounds, consistent with the observed

increase of the Si surface hydrophobicity. It appears that the $\text{Si}-(\text{OCH}_3)_x$ is formed by ArF laser induced decomposition of CH_3OH . This innovative technique of laser induced formation of a hydrophobic surface of Si (001), without AFM detectable surface morphology deterioration, is potentially attractive for in situ functionalization of Si wafers employed in the process of fabrication of microfluidic and lab-on-chip devices. We note that the same approach could be applied to fabricate highly hydrophilic surfaces of Si, and our preliminary experiments seem to confirm this expectation. Although we have not carried out repetitive wetting/dewetting experiments in this work, it is reasonable to expect that oxidized samples could be enriched with $\text{Si}-(\text{OCH}_3)_x$ if irradiated in methanol with the 193 nm laser. Thus, this research paves a new way to selective area in situ modification of Si surfaces from strongly hydrophobic to strongly hydrophilic and vice versa.

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