Dehydroxylation of UV Fused Silica Slides via UV Laser Irradiation

A J Fernandes[1], D M Kane[1], B Gong[2] and R N Lamb[2]

[1]Department of Physics, Macquarie University, Sydney, NSW 2109, Australia.
Contact Author Tel: +61-2-9850-6370; Fax: +61-2-9850-8115; Email: alanna@ics.mq.edu.au

[2]Surface Science and Technology, The University of New South Wales, Sydney, NSW 2052, Australia.

ABSTRACT

Further advances have been made in the development and understanding of an ultraviolet (UV) laser treatment of fused silica glass. Hydroxyl groups present on the surface can be removed by the treatment. The surface hydroxyl groups affect the surface adhesion [1] and performance of silica in catalysis, chromatography, photonics and microelectronics [2, 3]. This work shows that dehydroxylation via laser irradiation is a thermal process. An analysis technique using mass spectrometry has been developed to elucidate and avoid the effect of hydrocarbon contamination, allowing systematic measurements of dehydroxylation to be performed.

1. INTRODUCTION

Prior research has investigated the removal of contaminants from glass surfaces using UV laser irradiation. It was found that irradiation with a frequency-doubled copper vapour laser (255nm) caused removal of hydroxyl groups from the surface of high quality silica glasses [1]. This is known as 'dehydroxylation'. The significance of this is that these silanol (SiOH) groups are key sites in surface adhesion and bonding. Subsequently, micron and sub-micron sized particles were observed to adhere less well to the treated surface.

The dehydroxylation was quantified using Time-of-Flight Secondary Ion Mass Spectrometry (ToFSIMS) to compare the ratio of the $SiOH^+$ (at 45a.m.u.) and Si^+ (at 28a.m.u.) peaks before and after laser treatment. However, the results were difficult to reproduce. Further systematic study is presented here, which has shown the role of hydrocarbon contamination in masking of these peaks and the surface. A technique of sample preparation and analysis which minimises this effect has been developed. A KrF excimer laser (248nm, 12ns) was used to investigate the effects of laser repetition rate, laser fluence, and the total number of pulses used, on the dehydroxylation. This has led to the conclusion that the dehydroxylation via laser irradiation is a thermal process rather than a photochemical one.

2. EFFECT OF HYDROCARBON CONTAMINATION ON $SiOH^+/Si^+$ MEASUREMENTS

Experiments were undertaken to determine the surface hydroxyl density ($SiOH^+/Si^+$ ratio) of a clean UV fused silica sample, a hydrocarbon contaminated sample, and a laser treated dehydroxylated sample. Sample mounting and packaging for irradiation, storage and travel was also specially constructed to minimise contamination. The slides (UV 7980) were cleaned with a hydrogen peroxide (HP) process [4, 5], which is step 1 of the standard RCA wet cleaning technique for silicon. Immediate analysis of many samples by ToFSIMS, after cleaning, produced a $SiOH^+/Si^+$ ratio of 0.19±0.02 (see Figure 1a). This was taken as a reference value that is characteristic of the UV fused silica used (it may differ for other glasses). A surface was considered to be dehydroxylated if a ratio lower than the reference value was achieved (the lower the ratio, the greater the level of dehydroxylation achieved).

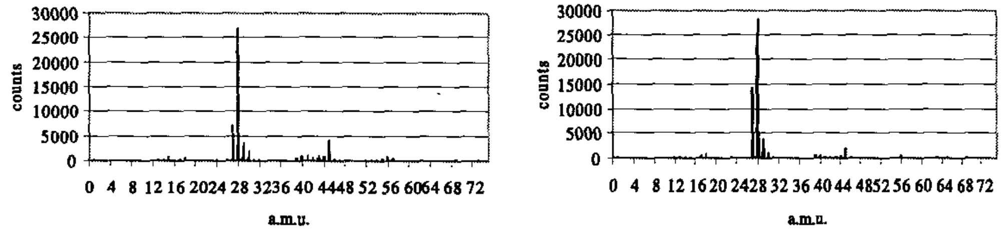

Figure 1: (a) non-irradiated HP cleaned, $SiOH^+/Si^+$ = 0.19; (b) dehydroxylated HP cleaned, $SiOH^+/Si^+$ = 0.09.

0-7803-7571-8/02/$17.00 ©2002 IEEE

Figure 1b is a typical spectra showing partial dehydroxylation of the surface. After laser irradiation, this sample was HP cleaned to remove hydrocarbon contamination, and analysed immediately. Note that although both Figures 1a and 1b show some hydrocarbon peaks, the contamination is minimal and does not mask the $SiOH^+$ and Si^+ peaks used in the analysis process.

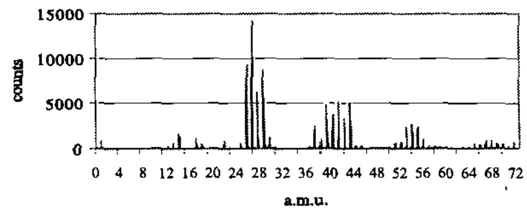

Figure 1: (c) hydrocarbon contaminated sample, $SiOH^+/Si^+$ ratio = 0.47.

In contrast, Figure 1c shows a typical spectrum for silica samples which were analysed after exposure for more than a day to air, without being HP cleaned. The spectra were dominated by hydrocarbons which masked the surface and caused the $SiOH^+/Si^+$ ratios measured to have much higher values up to 0.47. Such samples required cleaning using the hydrogen peroxide process to remove the hydrocarbons. This allowed samples which had already been laser irradiated to be analysed accurately. That is, the level of dehydroxylation was found experimentally not to be affected by the hydrogen peroxide cleaning process. It is not possible to use ToFSIMS quantitatively without this technique, as ToFSIMS measurements take several hours, and many samples irradiated in the same laser treatment run need to be analysed to find the dependency of dehydroxylation on laser fluence, pulse number, and repetition rate. The effect of hydrocarbon masking explains the irreproducibility in earlier results [1]. Systematic trends can be identified when this method is applied.

3. LASER TREATMENT FOR DEHYDROXYLATION OF SILICA

Figure 2 shows the experimental system for sample dehydroxylation using laser irradiation. A GSI Lumonics Pulsemaster 848 KrF excimer laser was used. The fluence (energy per unit area) was varied using an external Optec AT4030 attenuator, so that the irradiating energy could be changed without altering the beam area or focus.

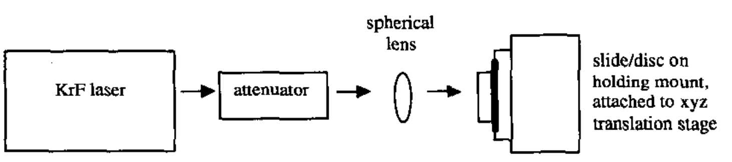

Figure 2: Experimental setup for sample irradiation in dehydroxylation experiments.

The beam was focussed to 3 x 7 mm^2 at the sample surface using a spherical lens of ~100mm focal length. A 20 x 10 mm^2 silica slide was attached to a translation stage, so that several regions could be irradiated. The pulse irradiation was applied with different pulse energies, number of pulses, and repetition rates, to investigate the effect on the dehydroxylation process.

4. DEHYDROXYLATION RESULTS

4.1 Dehydroxylation as a function of laser pulse fluence

The dehydroxylation achieved with varying single pulse laser fluence was examined. The fluences used ranged between 100 and 1200mJ/cm^2. The number of pulses used and the repetition rate of the laser were set to 400 and 20Hz respectively. Figure 3 shows the level of dehydroxylation achieved as the fluence is increased. The surface has become increasingly dehydroxylated as higher pulse fluence is applied.

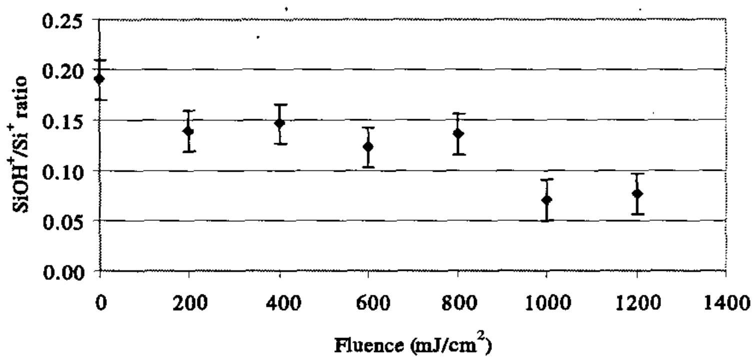

Figure 3: Dehydroxylation as a function of laser pulse fluence.

4.2. Dehydroxylation as a function of total fluence applied

This experiment investigated how the total fluence applied to the surface affected the level of dehydroxylation achieved. The total fluence incident on a given area was determined by the single pulse fluence multiplied by the number of pulses used. The total fluence was set to $360J/cm^2$, so that at lower fluences more pulses were used, and at higher fluences fewer pulses were used (for example, $400mJ/cm^2$ x 900 pulses, or $800mJ/cm^2$ x 450 pulses).

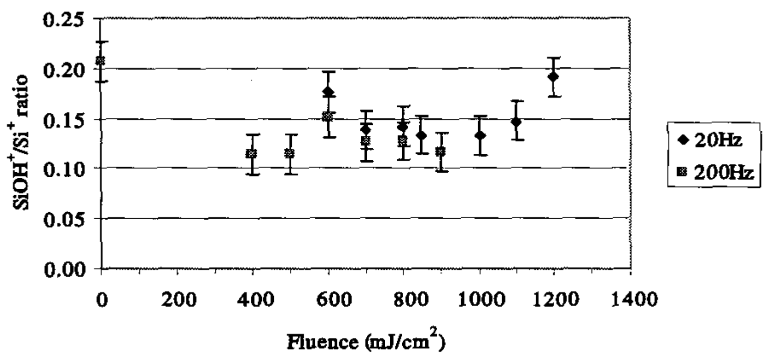

Figure 4: Dehydroxylation as a function of pulse fluence while total energy deposited is kept constant.

Figure 4 shows the dehydroxylation as a function of single pulse fluence, while keeping the total fluence deposited constant. This experiment was done at 20Hz and at 200Hz. A plateau region is observed at both repetition rates, indicating that if a given amount of thermal energy is deposited, a corresponding level of dehydroxylation is reached. Note that at 20Hz, if the single pulse fluence is too low, the energy again dissipates and less dehydroxylation is observed. At much higher fluences, damage to the surface is visually observed. This exposes regions of the glass which have not been treated by the irradiation, and are therefore not dehydroxylated. Thus, there is a window in which the laser parameters must be set to ensure dehydroxylation is measured for the laser treated silica.

At 200Hz the window of laser parameters causing dehydroxylation is wider than that at 20Hz. The fluence required for dehydroxylation has been lowered, and the base level of dehydroxylation has increased. This indicates that increased repetition rate assists the removal of the hydroxyl groups.

4.3. Dehydroxylation as a function of laser repetition rate

The effect of using laser repetition rates between 2 - 200Hz was tested. The fluence was set to 900mJ/cm^2, and the pulse number was 400. Figure 5 shows the level of dehydroxylation improves with increasing laser repetition rate, from which the following relationship can be observed:

$$\log (SiOH^+/Si^+ \text{ ratio}) = -0.71 \times \log (\text{repetition rate (Hz)}) - 0.48 \qquad (1)$$

The logarithm of the characteristic ratio for fused silica, log (0.19) = -0.72, corresponds to a threshold value of 6±2 Hz at which dehydroxylation begins to occur, using 900mJ/cm^2 & 400 pulses. At low repetition rates (below 10Hz) the energy dissipates too quickly to cause the cumulative heating effect needed for dehydroxylation to occur.

At 150Hz (2.18) and 200Hz (2.30) the level of hydroxyls increases again. This is due to optical damage occurring at these high repetition rates. Cracking and pitting of the surface was observed visually, exposing regions below the surface which had not been dehydroxylated.

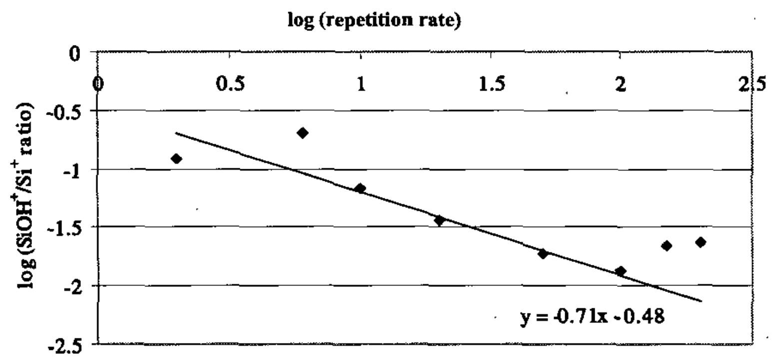

Figure 5: Dehydroxylation as a function of repetition rate.

5. CONCLUSION

The issue of hydrocarbon contamination must be considered carefully to establish a technique that allows for reproducible and quantifiable results to be obtained when measuring $SiOH^+/Si^+$ ratios on silica surfaces by ToFSIMS. By using a hydrogen peroxide wet clean, samples which have been subject to normal hydrocarbon contamination can be restored, without affecting the level of dehydroxylation achieved by laser treatment.

For a given energy, the dehydroxylation of the UV fused silica samples is improved as the laser repetition rate is increased, up to the point where optical damage occurs. This proves that the dehydroxylation of UV fused silica samples via laser irradiation is a thermal process. Care must be taken to ensure that irradiation occurs within certain operating windows, so that cumulative heating occurs, and optical damage is avoided.

REFERENCES

1. D.R. Halfpenny et al, Applied Physics A, **71** (2), 147-151, (2000).
2. S.P. Godfrey, J.P.S. Badyal and I.R. Little, J. Physical Chemistry B, **105** (13), 2572-2577, (2001).
3. A.S. D'Souza and C.G. Pantano, J. Am. Ceramic Society, **85** (6), 1499-1504, (2002).
4. SOP for RCA Clean, http://www.mines.edu/fs_home/cwolden/chen435/clean.htm (Accessed 31st October 2002).
5. RCA Clean, http://www.ece.gatech.edu/research/labs/vc/processes/rcaClean.html (Accessed 31st October 2002).