STUDY OF POST-DEPOSITION CONTAMINATION IN LOW-TEMPERATURE DEPOSITED POLYSILICON FILMS

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ABSTRACT

The presence of hydrogen in polysilicon films obtained at low temperatures by hot-wire CVD and the post-deposition oxidation by air-exposure of the films are studied in this paper. The experimental results from several characterization techniques (infrared spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry and wavelength dispersive spectroscopy) showed that hydrogen and oxygen are homogeneously distributed at grain boundaries throughout the depth of the films. Hydrogen is introduced during the growth process and its concentration is higher in samples deposited at lower temperatures. Oxygen diffuses along the grain boundaries and binds to Si atoms, mainly in Si_2O groups.

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1. INTRODUCTION

The role of grain boundaries (GB) in polycrystalline silicon (poly-Si) thin films is a key subject in the optimization of their behaviour in solar cells and other optoelectronic devices, since their electronic properties are dominated by localized states present at the GB [1]. The post-deposition hydrogenation of poly-Si films has been shown to improve their optoelectronic properties [2]. In addition, oxygen, which can easily penetrate in the polycrystalline structure through the GB when samples are exposed to air, could play an important role in the performance of poly-Si based devices.

Hot-wire chemical vapour deposition (HWCVD) has recently arisen as a technique which permits the deposition of poly-Si films at low temperatures, high growth rates and with a relatively large (~ 1 μm) crystallite sizes [3]. Moreover, this technique has also been used for the H passivation of Si surfaces [4]. Thus the understanding of the GB in poly-Si films produced by this technique is interesting for its application both in deposition and in post-deposition treatments of this material.

In this paper we focus on the study of H incorporated during the growth process of poly-Si films by HWCVD and their post-deposition oxidation by prolonged air-exposure. Infrared spectroscopy (IRS), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and wavelength dispersive spectroscopy (WDS) were used to study the presence of H and O impurities in air-exposed films.

2. EXPERIMENTAL

Four poly-Si samples were deposited by HWCVD in a reactor described elsewhere [3], using a tungsten filament, 1 mm thick and 150 mm long, which was heated to 1600°C as measured by an optical pyrometer. The distance from the filament to the substrates was varied, giving different substrate temperatures and growth rates, as shown in Table I. The gas phase composition was obtained from the mixture of 2 sccm of SiH_4 and 18 sccm of H_2, and total pressure in the reaction chamber was kept at 21 Pa. Fused silica and crystalline silicon (*c*-Si) wafers were used as substrates. The native oxide layer was left on *c*-Si substrates.

The thicknesses were measured by a Dektak profilometer and from scanning electron microscopy (SEM) cross-section images [3]. The IRS measurements were carried out in a BOMEM DA3 spectrometer with a 2 cm^{-1} resolution. A monochromatic X-ray Al source was used for XPS measurements in a Perkin Elmer PHI 5500 ESCA system. SIMS depth profiles were performed in an Atomika A-DIDA 3000-30 system by using Ar^+ ions as primary beam. The ions were accelerated to 15 keV with a primary ion current of 500 nA. WDS was used to obtain Si and O concentration line scans by using a 6 keV electron beam and a probe current of 3 nA.

3. RESULTS AND DISCUSSION

The structure of the present films has been studied in a previous paper [3] by X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). The films presented a columnar crystalline structure with 0.3-1 μm crystallite sizes and preferential orientation in direction [220]. No amorphous phase was detected in these samples.

IRS was used to study the H bonding in our samples. The samples were analyzed immediately after deposition, and after several weeks of air exposure. In Fig. 1, the transmittance spectrum of as-deposited sample HW4, and those of all samples after air exposure are presented. All the spectra were normalized to the thickness of the samples to allow comparison.

In as-deposited film (i.e., deposited and immediately characterized by IRS) two narrow stretching bands centered at 2100 and 2083 cm^{-1} appear. These two bands are respectively attributed to $=SiH_2$ groups passivating the GB and $-(SiH_2)_2-$ groups interconnecting different grains [5]. This indicates that HWCVD allows the incorporation of H in the film during the growth process.

The samples underwent substantial changes due to air exposure. First, the two narrow stretching bands observed at 2100 and 2083 cm^{-1} in as-deposited sample disappeared, and a wider band centered at 2100 cm^{-1} arose. In addition, a wide band appeared at 2250 cm^{-1}, which is attributed to Si-H bonds when Si atoms are bonded to O atoms [5].

Other important changes come from the bands between 1080 and 1240 cm^{-1}, related to the Si-O-Si antisymmetric stretching mode [6]. The higher frequency peak is attributed in this reference to the stress in the interface between the oxide and the Si matrix. These bands increased considerably after several weeks of air exposure, showing absorption levels much higher than the typically obtained from the top oxide surface layer in the case of c-Si wafers [6]. This fact suggests that our films contained a large amount of O incorporated through the GB. Moreover, the higher oxidation level occurs in the samples deposited at lower temperatures, corresponding to those which presented smaller grain sizes, and consequently higher GB surfaces, as we have reported in a previous paper from SEM analysis [3]. This result is also in agreement with the idea that the oxidation occurs mainly in the GB.

The relative weight of the higher frequency contribution with respect to the lower one in Si-O-Si bands was more important for the films deposited at higher temperatures. This behaviour could be related to some structural feature of the samples that changes when varying the deposition temperature.

Another band arose at 1720 cm^{-1} in air-exposed films, which was more intense in the films deposited at lower temperatures. This band has been attributed in the literature in the case of *c*-Si to interstitial O [7].

To study the post-deposition oxidation of our samples, the chemical state of Si atoms was studied by XPS analysis. Unfortunately, the sample HW2, which presented a clearly lower O content as deduced from IR spectra, could not be measured. All samples were analyzed after air-exposure, but their surface was cleaned *in situ* by Ar sputtering before being measured. The O/Si ratio in the films was estimated from the Si 2p and O 1s core level peaks, and was found to range between 0.12 and 0.15 in the three samples analyzed. Although some O implantation due to the sputtering cleaning cannot be ruled out, this contribution to the O content in the film is expected to be negligible, taking into account that if the same sputtering process is applied to a *c*-Si wafer, no O signal can be observed. The chemical state of Si was studied by the analysis of the Si 2p core level peak. Five components corresponding to $2p_{1/2}$ and $2p_{3/2}$ levels and to Si in +1, +2 and +3 oxidation states were used to fit the experimental data. No SiO_2 contribution (103.5 eV) was detected in these sputtering cleaned samples. In Fig. 2 the fit for the Si 2p peak of sample HW5 is presented. The relative weight of the Si^{+1} state was found to be 63% of the oxidized Si atoms for all the samples studied. The weight of the other oxidized states is very sensitive to the choice of the background and an accurate estimation is very difficult to obtain. The dominance of the Si^{+1} state, which corresponds to Si_2O bonds, agrees with the attribution of the IRS observed Si-O-Si related modes.

The H and O depth profiles were analyzed by SIMS. Higher H and O signal levels were found in samples deposited at lower temperatures. This corroborates the results observed by IRS. The decrease in the O signal in the films deposited at higher temperatures could be correlated to the larger crystallite sizes in these films. The smaller crystallite sizes in the samples deposited at lower temperatures increase the GB surface. This yields to a higher oxidized volume fraction in the film. As far as H is concerned, although the higher presence of GB in the samples deposited at low temperatures could favour a higher incorporation of hydrogen, the dramatic decrease in the H signal of the sample deposited at 500°C suggests that this behaviour is a consequence of temperature-activated desorption during the growth process.

The depth profiles of these elements in sample HW3 are presented in Fig. 3. The SIMS signal, which is the average for a surface that covers a great ammount of grains, is constant along the depth of the film. In the case of H this could be expected since it is incorporated in the film during the growth process. The homogeneous distribution of O through the depth of the films confirms that the oxidation of our poly-Si films is produced along the GB. The columnar structure of these films enhances the O diffusion along the whole depth of the film.

To obtain a more detailed portrait of the O incorporation in our films, several line scans were performed on all the films by WDS. Due to the spatial resolution and the charge effects, the grain sizes of our films could not be satisfactorily resolved in 2-D mapping. However, the use of 1-D scans minimized the charge effects and allowed us to obtain the Si and O concentration profiles along the surface of the films. In all cases the minima in Si signal corresponded to maxima in O signal and occured in the GB seen in the SEM image. In figure 4 a WDS line scan corresponding to sample HW2 is presented.

4. CONCLUSIONS

The results presented showed that some H in the form of Si-H bonds is present at the GB of poly-Si films deposited by HWCVD at low temperatures. The H content increases as the deposition temperature is lowered. The films become oxidized after several weeks of air exposure, as showed by the changes in the Si-H stretching band (~2100 cm^{-1}) and the increase in the Si-O-Si bands (1080-1240 cm^{-1}). O is absorbed after several weeks of air-exposure and diffuses through the GB giving an homogeneous depth profile through the films. This effect is enhanced by the columnar structure of our films. The degree of oxidation seems to be higher in the samples deposited at lower temperatures, which also presented smaller grain sizes and consequently a larger surface of GB. The O atoms are mainly in Si_2O bonds as deduced from the observed IR active bands and from the components of the Si 2p core level peak. The role of the GB in favouring the O diffusion has also been evidenced by the results from WDS showing an accumulation of O in the GB.

Finally, the incorporation of H during the growth process in HWCVD poly-Si films deposited at low temperatures, and the possibility of applying a post-deposition hydrogenation treatment in the same reactor opens unique possibilities to study the passivation of GB by H atoms and its influence on the post-deposition oxidation. Further work in this direction is being carried out.

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Figure captions

Figure 1. IRS transmittance spectra of the deposited samples. All the spectra have been normalized to the thickness of the samples. For the sample HW4, the spectrum of the as-deposited sample is also presented.

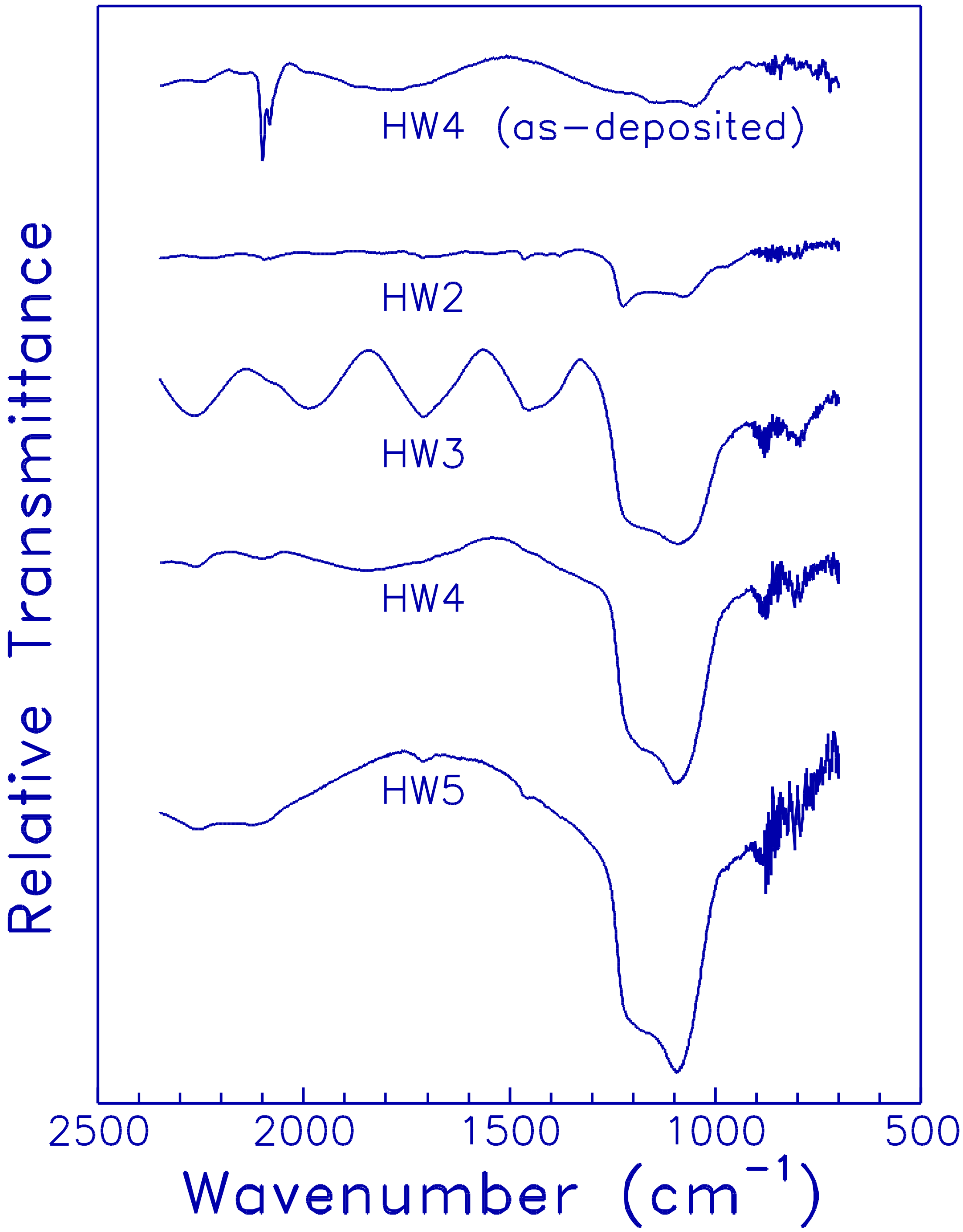
Figure 2. Measured Si 2p core level peak corresponding to the sample HW5, its fitting and the peaks used in it.

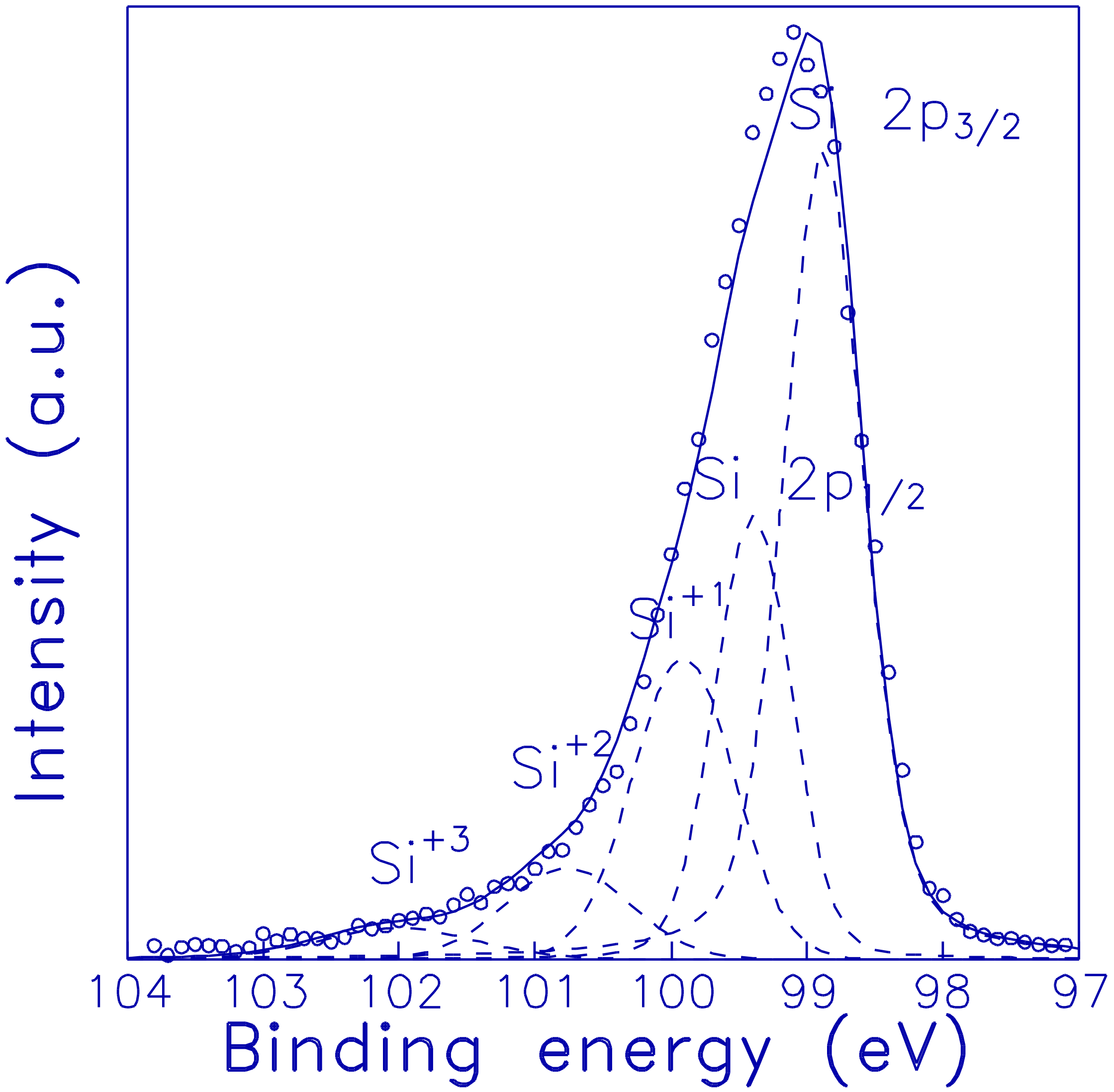
Figure 3. SIMS depth profile of sample HW3.

Figure 4. Surface silicon and oxygen signals as detected by WDS along a line scan of 10 μm of sample HW2. The O signal has been scaled up for better comparison.

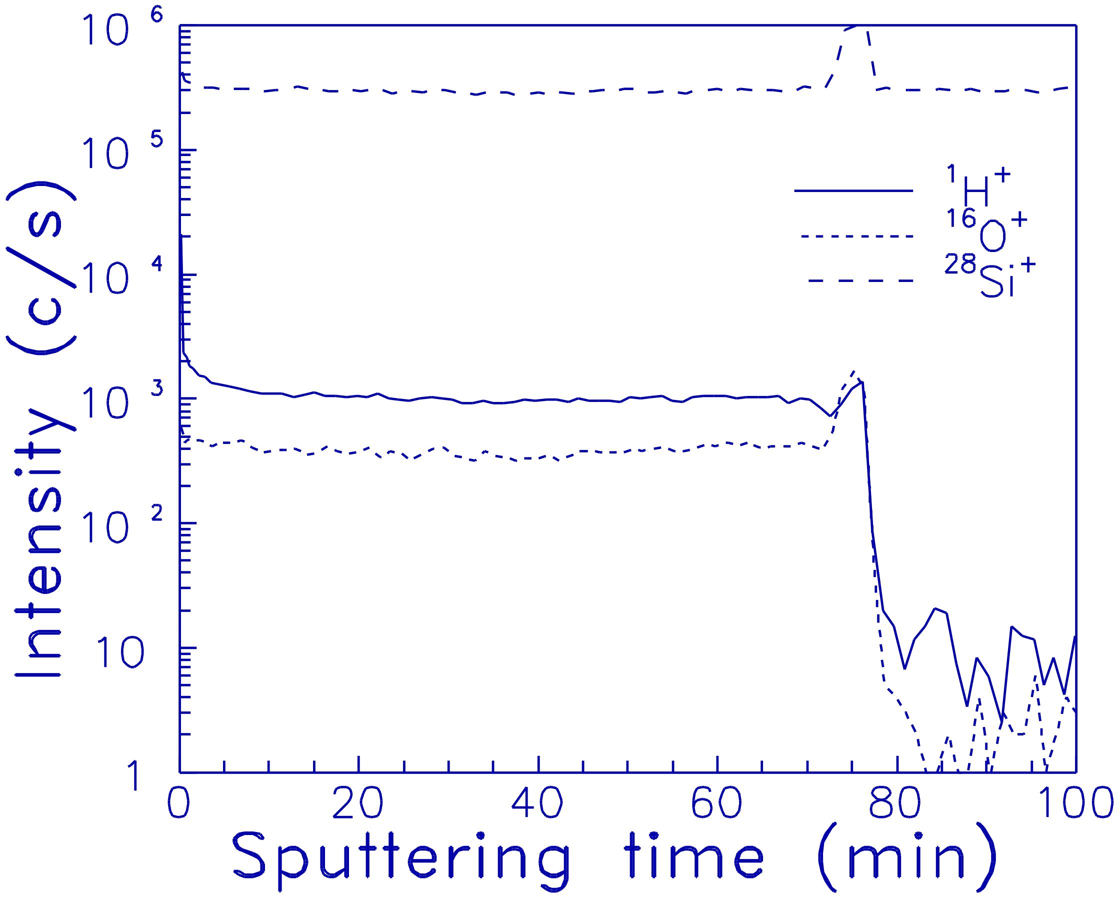
Table I. Deposition parameters: distance from substrate to filament (*d*), substrate temperature (T_s), thickness of deposited films (*t*) and deposition rate (r_d).

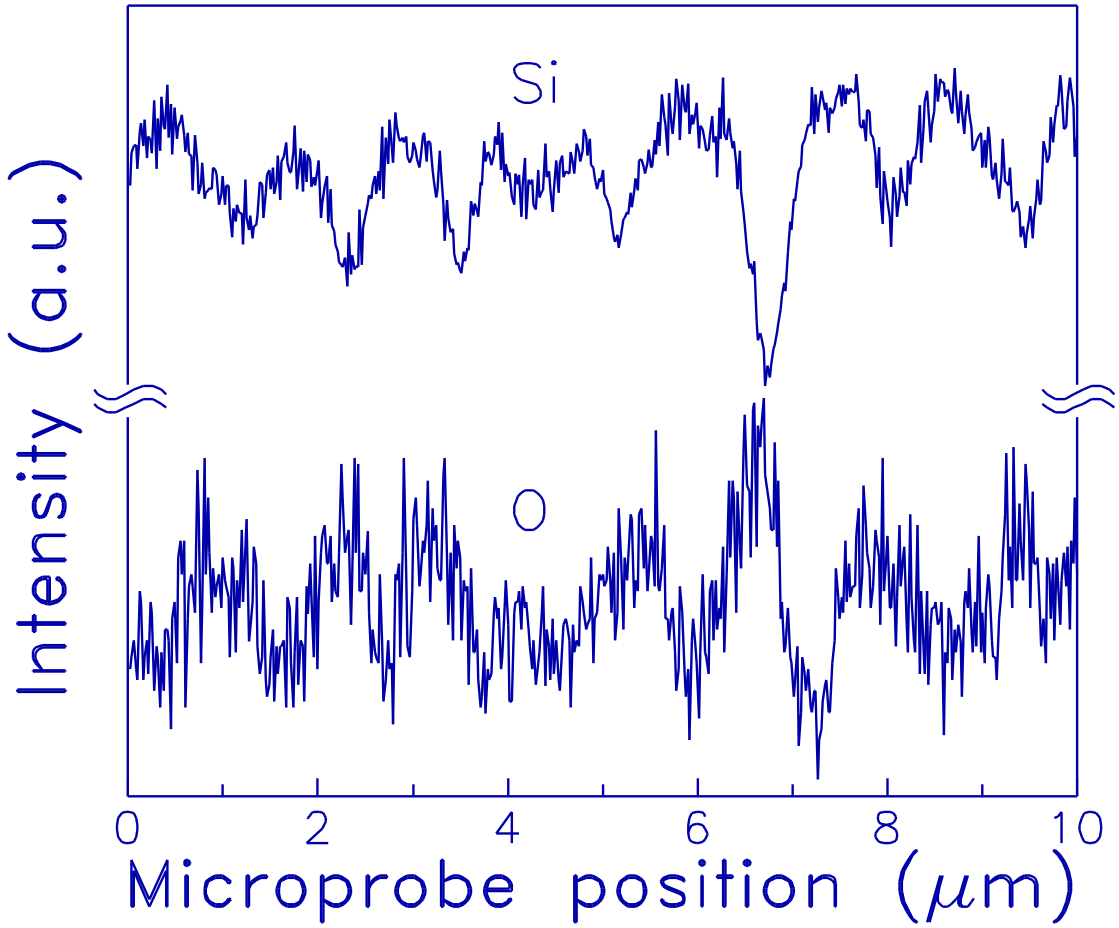
Sample	d (cm)	T_s (°C)	t (μm)	r_d (Å/s)
HW2	1	500	7.8	37.1
HW3	2	400	4.8	22.8
HW4	3	330	3.2	15.2
HW5	4	280	2.0	9.5


HW4 (as-deposited)
HW2
HW3
HW4
HW5
Relative Transmittance
2500
2000
1500
1000
500
Wavenumber (cm^{-1})



Intensity (a.u.)
Binding energy (eV)
104
103
102
101
100
99
98
97
Si 2p$_{3/2}$
Si 2p$_{1/2}$
Si^{+1}
Si^{+2}
Si^{+3}


Intensity (c/s)
10^6
10^5
10^4
10^3
10^2
10
1
0
20
40
60
80
100
Sputtering time (min)
$^{1}H^{+}$
$^{16}O^{+}$
$^{28}Si^{+}$


Si
O
Intensity (a.u.)
0
2
4
6
8
10
Microprobe position (μm)