

ADSORPTION OF OXYGEN, CAESIUM AND SODIUM ATOMS ON Si(100) SURFACE: EFFECT OF TEMPERATURE INDUCED BY A PULSED-LASER BEAM

M. Djabi, O. Benkherourou, J. -P. Deville^a

Institut de Physique, Université F. Abbas de Sétif - DZ - 19000, Algeria.

^aIPCMS - UMR 7504 - 23, rue du Loess 67037 Strasbourg Cedex, France.

The Second Harmonic Generation (SHG) technique was used to study the adsorption of alkali metals (Cs, Na) and oxygen on Si(100) surfaces. The SHG signal evolves regularly during sodium and oxygen adsorption. On the contrary, during caesium deposition it remains practically constant. In order to explain these phenomena, the approximate temperatures induced by the incident laser beam on the silicon surface have been calculated. It is shown that they can reach several hundred degrees. Weakly bound atoms can be thus desorbed during the analysis.

(Received April 3, 2000; accepted after revision May 22, 2000)

Keywords: Surface adsorption, Alkali metal atoms, Pulsed-laser beam

1. Introduction

A pulsed Nd-YAG laser was used to follow the adsorption of oxygen and alkali metals on Si(100) surfaces by studying the second harmonic signal as a function of time. A laser beam, of fundamental frequency ω , is directed on the sample surface and the 2ω component in the reflected beam due to the Second Harmonic Generation process [1-12] is recorded continuously during the adsorption. It is known that the symmetry breaking at the surface allows to be sensitive to surface modifications and even if the exact derivation of the SHG intensity is still difficult and controversial SHG could afford means of investigating adsorption – desorption processes.

During the interaction of the laser beam with the sample, part of its energy is absorbed in the sample. Consequently this induces a temperature increase at the surface [13,14], large enough to allow the desorption of weakly bound atoms. In a previous paper, it has been shown that, in the case of a tungsten surface, the increase of temperatures is very important [15].

The aim of this work is to determine the temperature induced by the laser beam interaction. If it is in the expected range of thermal desorption, the adsorption process of atoms such as O, Cs and Na on silicon surfaces will be impossible to be detected by SHG techniques. On the other hand, SHG could be then useful to investigate desorption kinetics if one is able to have a good approximation of the temperature as a function of time.

2. Experimental procedure

All the experiments were performed in an ultrahigh vacuum chamber maintained at a base pressure 5×10^{-10} mbar. The chamber is also equipped with a retarding field analyser (RFA) for Auger electron spectroscopy (AES) in order to achieve surface analysis. The Si(100) surface was cleaned *in-situ* by repeated heating cycles at 750 °C immediately followed by annealing at 1100 °C during 30 seconds. SHG from Si(111) surfaces could be monitored during alkali metal deposition performed from SAES getters used as alkali sources. The second harmonic measurement was carried out with a

pulsed Nd-YAG laser beam at $\lambda = 1.064 \mu\text{m}$ with p polarisation at a repetition rate of 10 Hz. The incident pulse energy was typically 6 to 8 mJ per pulse (pulse width: 15 ns). The incident angle was kept equal to 45° . The laser beam diameter on the surface is equal to 4 mm. The second harmonic signal with selected p polarisation was detected after proper filtering *via* a photomultiplier tube and then processed through a gated electronic system.

3. Results

The results obtained by SHG technique on the Si(100) surface during O, Cs and Na adsorption are presented in Figs. 1, 2 and 3 respectively.

3.1. Oxygen adsorption on Si(100)

The clean Si(100) surface has been exposed to an oxygen pressure of 10^{-7} mbar. The SHG $I(2\omega)$ signal decreases rapidly and after 75 seconds falls below the detection level (Fig. 1).

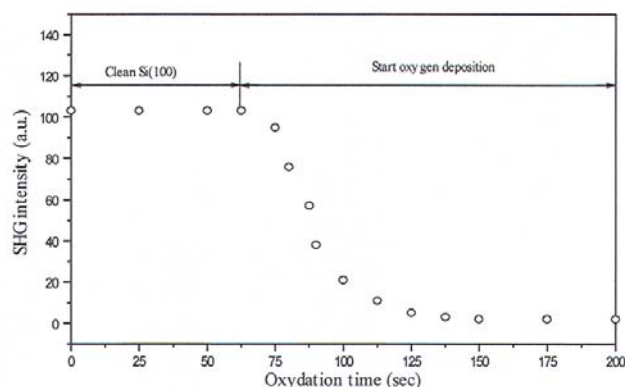


Fig. 1. S.H.G. signal from Si(100) surface during oxidation procedure.

3.2. Cs adsorption on Si(100)

The $I(2\omega)$ signal from the Si(100) surface is monitored continuously as a function of time during Cs evaporation from the SAES getter source. As seen in Fig. 2, it remains constant before opening the shutter, then as soon as the evaporation begins it starts to decrease and reaches a minimum after an evaporation of 30 seconds. The signal is then approximately 40 % of the one relative to the clean Si(100) surface. Continuing the Cs evaporation the signal increases slightly and reaches a constant value which is about 15% of the one relative to clean silicon. The SHG signal is thus not directly related to the supposed amount of Cs deposited.

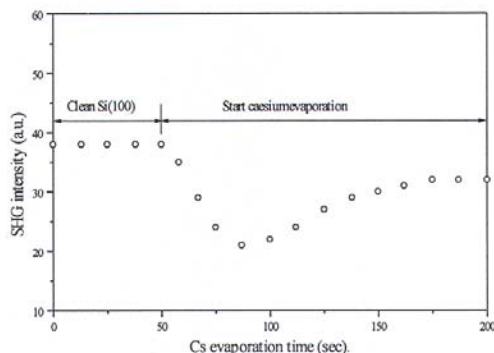


Fig. 2. S.H.G. signal during Cs adsorption atoms on Si(100) surface.

3.3 Na adsorption on Si(100)

In the case of sodium deposition, the second harmonic $I(2\omega)$ signal from the Si(100) surface increases steadily with the evaporation time (Fig. 3).

Then the Na/Si(100) system was kept exposed to the laser beam without further Na deposition and the $I(2\omega)$ signal remained constant for a long time (not shown on the figure). In this case, it is clear that the laser beam does not desorb the sodium atoms.

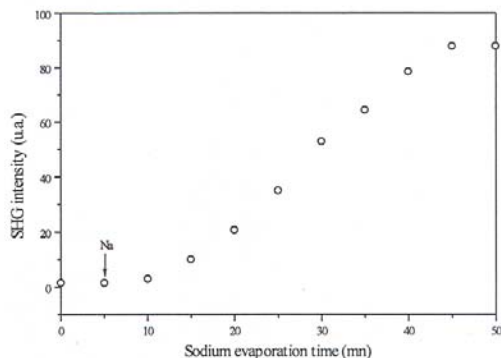


Fig.3. S.H.G. signal during Na adsorption atoms on Si(100).

4. Discussion

The clean Si(100) surface always generates a second harmonic signal $I(2\omega)$ and, during exposure to an oxygen atmosphere, this signal drops very quickly. Indeed, oxygen is an electron acceptor and reduces the surface electron density. This explains the fast decrease of the SHG signal which is characteristic of clean metal surfaces exposed to electronegative molecules, as described in references [16-21].

During caesium adsorption, the $I(2\omega)$ signal decreases only at the beginning of the deposition and then increases. 40 % of this decrease could be due, like in the Cs/W(100) system [22], to contaminants trapped by a getter effect of the caesium atoms at the beginning of the deposition. The slight increase of second harmonic $I(2\omega)$ signal which follows can be explained by the effect of caesium adsorption [23-24]. One could expect that the $I(2\omega)$ signal would still increase [23], however

it kept constant. Two hypotheses can be made: either the coverage does not increase beyond one monolayer due to the saturation of the dangling bonds of silicon or caesium atoms do not stick at the surface and are desorbed with some contaminants due the effect of the laser beam. Similarly to the case of tungsten surfaces [15], the temperature induced by the incident laser beam on the silicon surface can be very high and may favour the fast desorption of caesium atoms.

Contrary to the case of caesium, the adsorption of sodium atoms on Si(100) surface has been detected by SHG signal. At the beginning of the sodium deposition, the variation of the S.H. signal with time is very weak. For $t > 10$ minutes, the S.H. signal increases greatly with deposition time and after $t = 40$ minutes, it reaches a constant value. According to Spiess [25] and taking into account the pressure during the sodium deposition: $(5 \div 8) \times 10^{-10}$ mbar, two sodium monolayers are deposited on Si(100) surface. The constant value of the S.H. signal corresponds to the second monolayer [26], no specific S.H. signal has been observed at the completion of the first monolayer, probably because of contaminants such as oxygen. It has been shown that alkali overlayers on surfaces are highly sensitive to oxygen adsorption [27] and that oxygen could induce significant changes in the second harmonic generation.

When the sodium evaporation is stopped, the $I(2\omega)$ signal remains at the same value. The bond between sodium and silicon is thought to be stronger than for caesium and the temperature increase due to the laser beam is not high enough to allow sodium or oxygen desorption.

To confirm these hypotheses, an evaluation of the temperature increase due to the laser beam impinging on the Si(100) surface has been performed.

The intensity of radiation when it interacts with matter (here the silicon surface) decreases following a Lambert-Beer law [28]:

$$I(r) = I_0 \exp\left(\frac{-2\omega n\kappa}{c} r\right) = I_0 \exp(-\chi r) \quad (1)$$

where χ represents the absorption coefficient, r the travel distance, c the speed of light, ω the frequency of the radiation, n , the real part of the refraction index and k , the attenuation index (or extinction coefficient) which is the imaginary part of the refraction index:

$$\chi = \frac{2\omega n\kappa}{c} = \frac{4\pi\kappa}{\lambda} \text{ where } \lambda \text{ is the wavelength in the medium.} \quad (2)$$

$I(r)$ is decreased of $1/e$ of its initial value each time the radiation travels in the solid a distance equal to r_0 :

$$I(r_0) = \frac{I_0}{e} \Rightarrow r_0 = \frac{\lambda}{4\pi\kappa} \quad (3)$$

r_0 is known as the skin depth or penetration depth.

The penetration depth of the laser beam inside the sample, along the normal to the surface, is:

$$y_0 = r_0 \cos \alpha = \frac{\lambda}{4\pi\kappa} \cos \alpha \quad (4)$$

The refraction angle α is determined from the Snell - Descartes law:

$$\sin \theta = n \sin \alpha \quad (5)$$

To determine the temperatures induced by the laser beam, one should take into account that, when the laser radiation impinges on the sample surface, part of its energy W_0 , called W_{ref} , is reflected, another part is absorbed as heat ΔQ further denoted as W_{abs} . The quantity of energy absorbed by the solid upon a distance y_0 is W_{abs} :

$$W_{\text{abs}} = W_0 - W_{\text{ref}} = \Delta Q = m \int C_p dT \quad (6)$$

Here W_0 is the total laser energy, m is the quantity of material which has absorbed the energy in the volume V , C_p being the heat capacity. This absorbed energy W_{abs} can be written as:

$$W_{\text{abs}} = 2/3 (1 - R) W_0 \quad (7)$$

where R is the reflection coefficient of the solid and where the constant $2/3$ stands for the value $2/e$ (since $e \approx 3$) which can be explained by the fact that $1/3$ of the energy transmitted to the solid penetrates the bulk of the solid, beyond the skin depth.

The incident laser beam has a circular section and at the sample surface with a diameter d , the spot becomes elliptical with a great axis D . The sample volume in which the energy is absorbed is $V=Ay_0$ where A is the area of the spot having an elliptical shape. So:

$$A = \frac{\pi d^2}{4 \cos \theta} \Rightarrow V = \frac{\pi d^2}{4} \frac{\lambda \cos \alpha}{4\pi \kappa \cos \theta} \quad (8)$$

The mass contained in the volume V is given by:

$$m = \rho V = \rho \frac{d^2 \lambda \cos \alpha}{16 \kappa \cos \theta} \quad (9)$$

If C_p can be written as $C_p = a + bT$ where a and b are constants, relation (7) becomes:

$$m \frac{b}{2} T_f^2 + maT_f - \frac{2}{3}(1-R)W_0 - maT_0 - m \frac{b}{2} T_0^2 = 0 \quad (10)$$

T_0 is the initial temperature of the Si(100) surface just before the laser pulse, *i.e.* the ambient temperature, and T_f is the temperature just after the laser pulse, *i.e.* the temperature induced by the laser beam.

By solving equation (10) one obtains the increase of temperature at the surface of the sample during the laser pulse. For this purpose one has to take into account the physical parameters relative to the laser beam and the silicon substrate:

– Laser beam:

* wavelength $\lambda = 1.064 \mu\text{m}$; beam diameter $d = 4 \text{ mm}$; energy $W_0 = (1 \div 10) \text{ mJ}$; incidence angles: $30^\circ, 45^\circ, 60^\circ$ (three angles have been considered in the calculations although experiments were performed at 45°).

– Silicon:

* depth penetration at $\lambda = 1.064 \mu\text{m}$: $r_0 = 1 \mu\text{m}$ [29]; coefficient of reflectivity at $\lambda = 1.064 \mu\text{m}$: $R = 28 \%$ [29]; thermal coefficients: $a \sim 850 \text{ J/kg.K}$, $b \sim 0.10 \text{ J/kg.K}$ [29]; refraction coefficient at $\lambda = 1.064 \mu\text{m}$: $n = 3,5$ [29].

For this data set, the derived temperatures induced by the pulsed-laser beam impinging on the silicon surface are given in Table I.

Table I: Temperatures induced by the pulsed-laser beam irradiation on a Si(100) surface.

W_0 (mJ)	$\theta = 30^\circ$	T_f (K)	
		$\theta = 45^\circ$	$\theta = 60^\circ$
1	315	311	308
2	330	325	317
3	347	338	327
4	363	352	337
5	379	365	346
6	395	378	356
7	411	391	365
8	427	405	375
9	443	418	384
10	459	432	394

Temperature increases up to 200 K can be observed for energies of about 10 mJ per pulse. This is much lower than the one observed in the case of tungsten substrates [15]. However they are still large enough to induce some thermal desorption for weakly bond molecules or atoms. The

differences in SHG signal evolution between oxygen, sodium and caesium adsorption should then be attributed to differences in bonding energy. It is clear that neither oxygen nor sodium desorption is induced by the laser beam, on the contrary for caesium atoms some desorption occurs.

4. Conclusion

Temperatures induced on the Si(100) surfaces by the laser beam used to do SHG experiments are relatively high and may induce the desorption of the caesium atoms during their deposition. However, they are not sufficient to desorb sodium and oxygen atoms and their adsorption leads to a clear SHG signal variation. This is, probably, because caesium is more volatile than sodium and because oxygen has a strong chemical bond with silicon, favoured by a temperature increase. It is also believed that deposition of alkali atoms such as caesium favours some getter effect, leading to a co-deposition of impurities at the surface. It shows that it is necessary to have an ultra-high vacuum better than 10^{-10} mbar, and a laser beam power in the range $1 \div 3$ mJ to obtain convincing SHG results when studying the adsorption of alkali atoms on silicon surfaces.

References

- [1] N. Bloembergen, *Non-linear Optics*, New-York, Benjamin (1977).
- [2] Y. R. Shen, *Principles of non-linear Optics*, New-York, Wiley (1984).
- [3] A. Liebsch, *Surf. Sci.*, **307**, 1007 (1994).
- [4] Y. R. Shen, *Surf. Sci.*, **299/300**, 551 (1994).
- [5] Y. R. Shen, *Appl. Phys.*, **A 59**, 541 (1994).
- [6] C. Yamada, T. Kimura, *Nonlinear Optics, Principles, Materials, Phenomena and Devices*, **12**, 137 (1995).
- [7] J. F. McGilp, *Progress Surf. Sci.*, **49**, 1 (1995).
- [8] J. F. McGilp, *J. Phys.*, **D 29**, 1812 (1996).
- [9] J. F. McGilp, *Thin Solid Films*, **313-314**, 533 (1998).
- [10] G. Lüpke, *Surf. Sci. Reports*, **35**, 75 (1999).
- [11] N. Bloembergen, *Appl. Phys. B, Lasers and Optics*, **68**, 299 (1999).
- [12] Y. R. Shen, *Appl. Phys. B, Lasers and Optics*, **68**, 295 (1999).
- [13] H. S. Carslaw, J. C. Jaeger, *Conduction of heat in solids*, Clarendon Press, Oxford University Press (1990).
- [14] T. Suzuki, A. Mikami, K. Uehara, M. O. Aono, *Surf. Sci.*, **323**, L 293 (1995).
- [15] M. Djabi, A. Fort, O. Benkherourou, J. -P. Deville, *Ann. Chim. Sci. Mat.*, **24**, 157 (1999).
- [16] H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, T. F. Heinz, G. A. Somorjai, Y. R. Shen, *Phys. Rev. Lett.*, **52**, 348 (1984).
- [17] H. W. K. Tom, X. D. Zhu, Y. R. Shen, G. A. Somorjai, *Surf. Sci.*, **167**, 167 (1986).
- [18] D. Heskett, L. E. Urbach, K. J. Stone, E. W. Plummer, H. L. Dai, *Surf. Sci.*, **197**, 225 (1988).
- [19] S. G. Grubb, M. D. DeSantolo, R. B. Hall, *J. Phys. Chem.*, **92**, 1419 (1988).
- [20] Z. Rosenzweig, M. M. Asscher, *Surf. Sci.*, **204**, L732 (1988).
- [21] K. Pederson, P. Morgen, *Phys. Rev.*, **B 53**, 9544 (1996).
- [22] C. A. Papageorgopoulos, J. M. Chen, *Surf. Sci.*, **39**, 283 (1973).
- [23] H. W. K. Tom, C. M. Mate, X. D. Zhu, J. E. Crowell, Y. R. Shen, G. A. Somorjai, *Surf. Sci.*, **172**, 466 (1986).
- [24] P. E. Hansen, K. Pedersen, L. Liu, P. Morgen, *Surf. Sci.*, **391**, 252 (1997).
- [25] L. Spiess, P. S. Mangat, S. P. Tang, K. M. Schirm, A. J. Freeman, P. Soukiassian, *Surf. Sci.*, **289**, L631 (1993).
- [26] J. Boness, G. Marowsky, J. Braun, G. Witte, H. G. Rubahn, *Surf. Sci.*, **402/404**, 51 (1998).
- [27] T. Götz, M. Buck, C. Dressler, F. Eisert, F. Träger, *Appl. Phys.*, **A 60**, 607 (1995).
- [28] M. Born, E. Wolf, *Principles of Optics*, New-York, 6th ed., Pergamon Press (1980).
- [29] R. C. Weast, M. J. Astle, W. H. Beyer, *CRC Handbook of Chemistry and Physics*, Boca Raton, Inc., Florida, 67th ed., CRC Press (1986-1987).