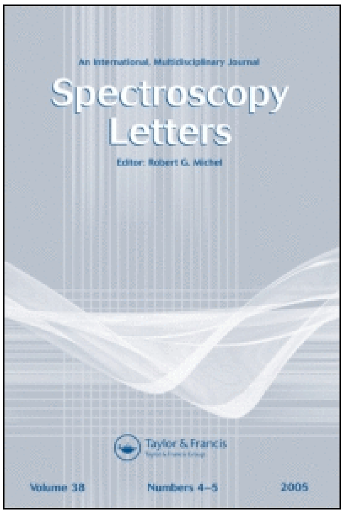

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Re-Investigation of the Raman Spectrum of D_2 Bombarded Si Surface

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RE-INVESTIGATION OF THE RAMAN SPECTRUM OF D_2^+ BOMBARDED Si SURFACE

KEY WORDS: Raman Scattering from implanted silicon

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ABSTRACT:- The Raman spectrum of the surface of a P-type <111> silicon wafer bombarded with 30 KeV D_2^+ has been re-investigated. The recorded spectrum not only confirms the formation of a-Si layer and various silicon, deuterium and hydrogen complexes, but enables the identification of others.

INTRODUCTION

The bombardment of a solid surface by energetic ions often results in the retention of some of the incident ions by the lattice of the solid target. The reaction of the incident ions with the lattice atoms, after the incident ions have come to rest in the lattice can contribute towards the chemical trapping of these ions. Chemical trapping can be evidenced by the appearance of local mode absorptions and scattering. In this paper we are reporting a re-investigation of the Raman spectrum

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of the silicon surface, which has been subjected to D_2^+ implantation. This study has been initiated by the fact that the bombarded surface can contain various forms of complex formations, which though have not been fully investigated, yet some characterizations have been observed (1,2).

EXPERIMENTAL

A linear accelerator* employing a duo-plasmatron ion source has been used to bombard a 25 mm diameter P-type single-crystal <111> cut silicon wafer properly cleaned, etched and polished. Dry CP grade deuterium gas (with some hydrogen as impurity) is used as ion-source feed-in material and 30 KeV D_2^+ ions are implanted in the sample. The total fluence is of the order of 10^{17} ions/cm^2. In order to achieve good vacuum ($\approx 10^{-7}$ mm Hg), a clean environment around the target area, and to prevent the deposition of pump oils, a liquid nitrogen cooled jacket around the target is used.

Raman studies on the implanted silicon surface were performed using the Surface-Raman facility at the University of Kentucky in Lexington (KY) USA. The sample wafer was mounted in an evacuated chamber and the 5145 Å line of the Ar^+ laser was allowed to illuminate a small part of the implanted area through a high pressure window.

Using the standard 90° geometry for Raman scattering, scattered radiation was collected by a collimating lens, and a cylindrical lens was used to transfer the Raman scattered radiation through another high pressure window on to the entrance slit of the Jarrell-Ash double monochromator. The monochromator was driven by a Burleigh-Piezoelectric Inchworm. The entire operation of the monochromator and the data

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* Linear Accelerator on loan from Leo Narodny, Barbados Optical Co.

acquisition by a photon counting technique is computer controlled. The data was stored on a disc and was transferred to a plotter for display as required. Average dark noise of the cooled photomultiplier during the 5 sec/step was of the order of 9 counts. Signals significantly higher than the background mentioned above were taken as real.

RESULTS AND DISCUSSION

It has been shown by Smith et al (3), Crowder et al (4) and Bourgoin et al (5) that the bombardment of crystalline silicon by a heavy dosage of ions ($\geq 10^{15}$ ions/cm^2) results in the formation of a continuous layer of amorphous silicon on crystalline surface. The inelastic light scattering from such a combination should contain both amorphous and crystalline silicon characteristics. This was confirmed by the simultaneous presence of a crystalline silicon peak at 522 cm^{-1} as well as a-Si peak at 480 cm^{-1} in the Raman spectrum (5). In our observations the presence of 485 and 522 Raman peaks confirms the existence of an a-Si layer on a crystalline Si surface. Gruen et al (6) reported the infrared and Raman active modes of D_2^+ implanted <111> Si wafer at 1390 and 1460 cm^{-1}, equivalent bands in our spectrum are at 1385 and 1470 cm^{-1} respectively.

The combination of amorphous and crystalline silicon is further subjected to D_2^+ bombardment resulting in the implantation of D_2^+ in both types of silicon, which in turn is expected to result in the formation of various complexes. Some of the characteristic activities of these complexes might be Raman active, and should be identifiable in the Raman spectrum of the surface of such a system. Also, exposure of silicon to atmosphere results in the formation of SiO_2 layer on the silicon surface, which should also be revealed in the Raman spectrum. The Raman bands observed in our study of D_2^+ implanted silicon are collected in Table 1

Table 1 - Raman Spectrum of D_2^+ implanted Silicon (comparison with the available data on silicon and silicon, oxygen, hydrogen and deuterium complexes).

A	B	C	D	E	F	G	H	I	J	K	L
a-Si	Cry-Si	SiO_2	SiO	Si_4H_4	Si_4D_4	Si_2H_6	Si_2D_6	B_2H_6	B_2D_6	B_2D_5H	D_2^+ imp-Si
$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$
		60									
			79								76
											87
		115^f									116
		147^e									147
		207^e									198
										260	238
							277^*				262
300											315
							352.8				358
380^a											375
		410					407.5				415
						434.5					434
					454						454
							474.4				474
480		490			490						488
	522										522
							559.4				563
									588		588
		600									609
630				637	639						635 = 2 x 315
				658	650						652
							667.0				674
							683.1				705

											750 = 2 x 735
			766								766
		800									805
							833.3				842
			850			842^g					850
				898							886
				906							906
						910					914
						935					
							951.6				952
											976 = 2 x 488
970											
						1000^h					996
											1070
		1065^d									
											1080
							1139.0				1136
								1180.4			1180
											1215
		1200									
						1244					1244
									1269		1258
											1346
							1364.3				1358
	1390^b										1385
							1446.6				1440
	1470^b										1470
							1490.7				1492

[A. Amorphous Silicon: Bourgoin _et al_ (5) a. Brodsky _et al_ (7)] [B. Crystalline Silicon: b. Gruen _et al_ (6)] [C. Hass _et al_ (8) d. Yadav _et al_ (11) e. Shapiro _et al_ (12); f. Pfeifter _et al_ (13)] [D. Hastie _et al_ (14)]
[E. Knights _et al_ (15)] [F. Knights _et al_ (15)] [G. Gutowski _et al_ (16) g. Lucovsky _et al_ (17) h. Bethke _et al_ (18)]
[H. Bethke _et al_ (18), *-IR band], [I. Lord _et al_ (19)] [J. Lord _et al_] [K. Lehmann _et al_ (20)] [L-OUR DATA].

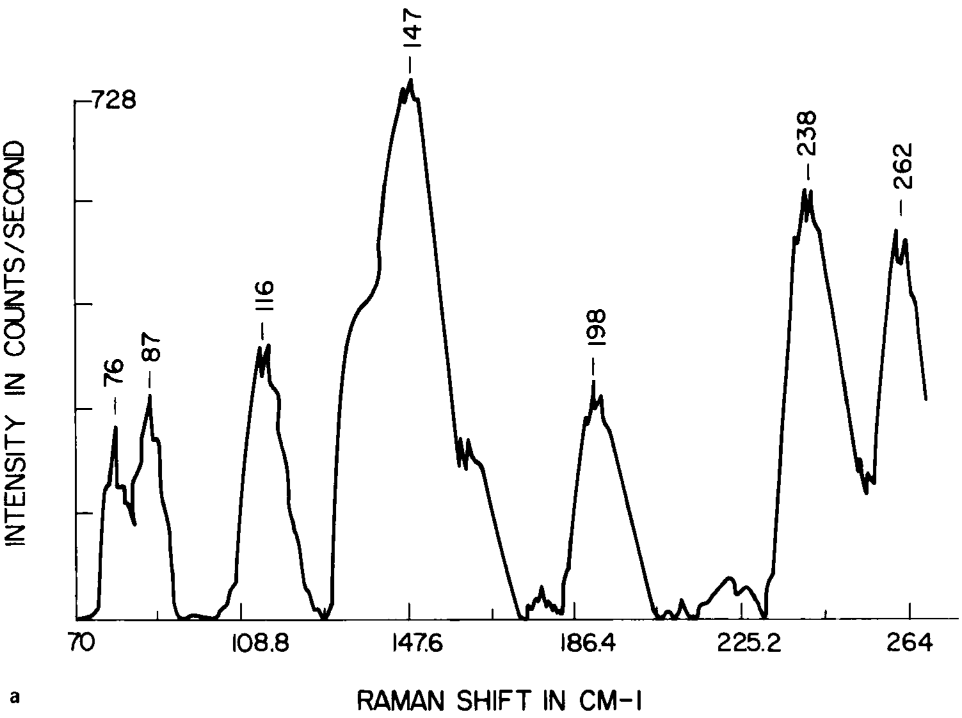

Fig. 1a

and are compared with the published IR and Raman data on D_2^+ implanted silicon. The Raman spectra of D_2^+ implanted crystalline silicon surface as recorded by us are displayed in Figures 1(a-e).

Smith et al (3) pointed out the presence of 480 and 300 cm^{-1} Raman bands and associated them with the transverse optical and longitudinal acoustic structures in a-Si. Corresponding bands in our observation are at 315 and 488 cm^{-1} and their overtones in the spectrum appear at 635 and 976 cm^{-1}. Following earlier observations of Brodsky et al (7), the 635 and the 976 cm^{-1} bands above can be labelled as ω_{2LA} and ω_{2TO}. Brodsky et al (7) also observed a Raman shoulder at 380 cm^{-1} and assigned it to the longitudinal optical structure ω_{LO} in a-Si, we are observing

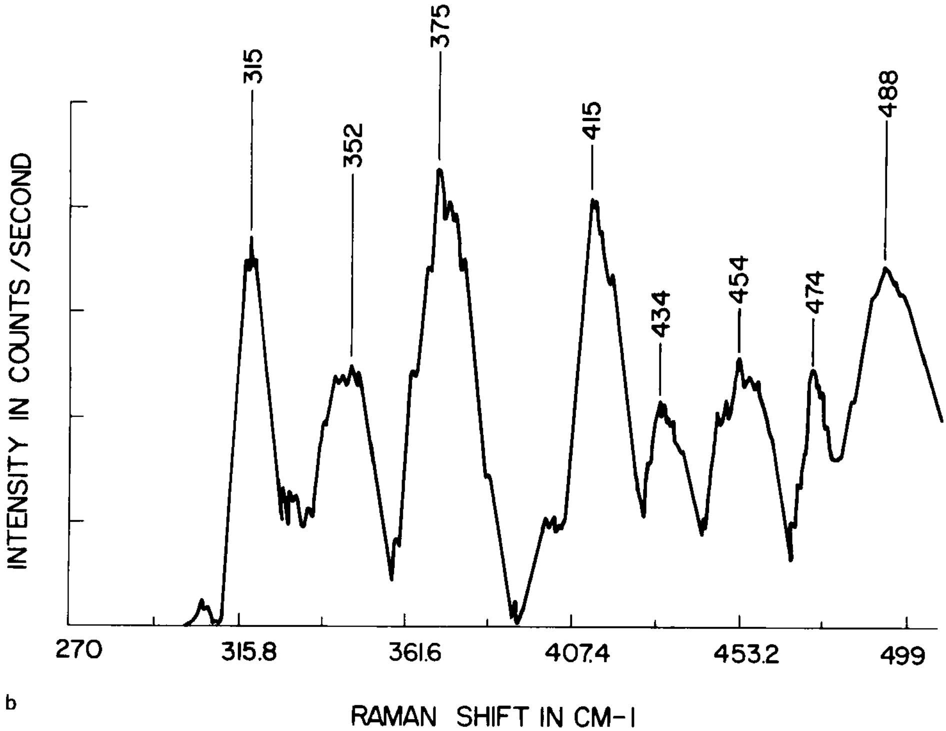

Fig. 1b

the corresponding band at 375 cm^{-1} and the 750 cm^{-1} band is its overtone.

Hass (8) reported the Raman spectra of SiO_2 in the 10 - 1300 cm^{-1} region and observed bands at 60, 410, 490, 600, 800, 1065, and 1200 cm^{-1}. The 410 cm^{-1} Raman band above with an IR counterpart at 443 cm^{-1} is associated with a 'bond-rocking' motion in which atoms move roughly perpendicular to Si-O-Si planes, and has it equivalent in our study at 415 cm^{-1}. The 800 cm^{-1} Raman band in SiO_2 spectrum of Hass, as mentioned above, has been associated with the 'bond-rocking' type of motion in which the oxygen moves approximately at 90° to Si-Si lines in Si-O-Si

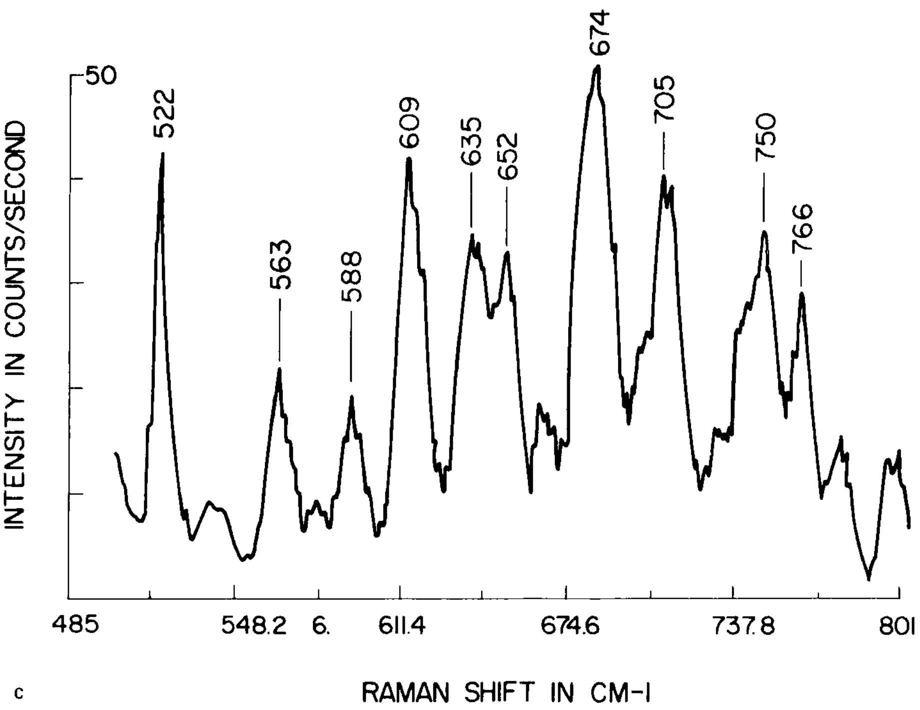

Fig. 1c

planes. This mode was calculated by Lippincott et al (9) to be at 730 cm^{-1}. In our study this bands appears at 805 cm^{-1}. The bond stretching vibration in SiO_2 in which the bridging oxygens move in opposite directions to their Si neighbours, and roughly parallel to Si-Si lines, was assigned by Hass (8) to the 1067 cm^{-1} Raman band. In our study the 1080 cm^{-1} component of the 1070 cm^{-1} doublet could be the equivalent 'bond-stretching' vibration. Hass (8) also observed bands at 490 and 600 cm^{-1}, which were not assigned. The 600 cm^{-1} Raman band above appears at 609 cm^{-1} in our study, and the 490 cm^{-1} (our 488 cm^{-1}) band has been assigned and discussed earlier. The 1200 cm^{-1} Raman band of SiO_2 as reported by Hass (8) has it equivalent in our spectrum of 1215 cm^{-1}.

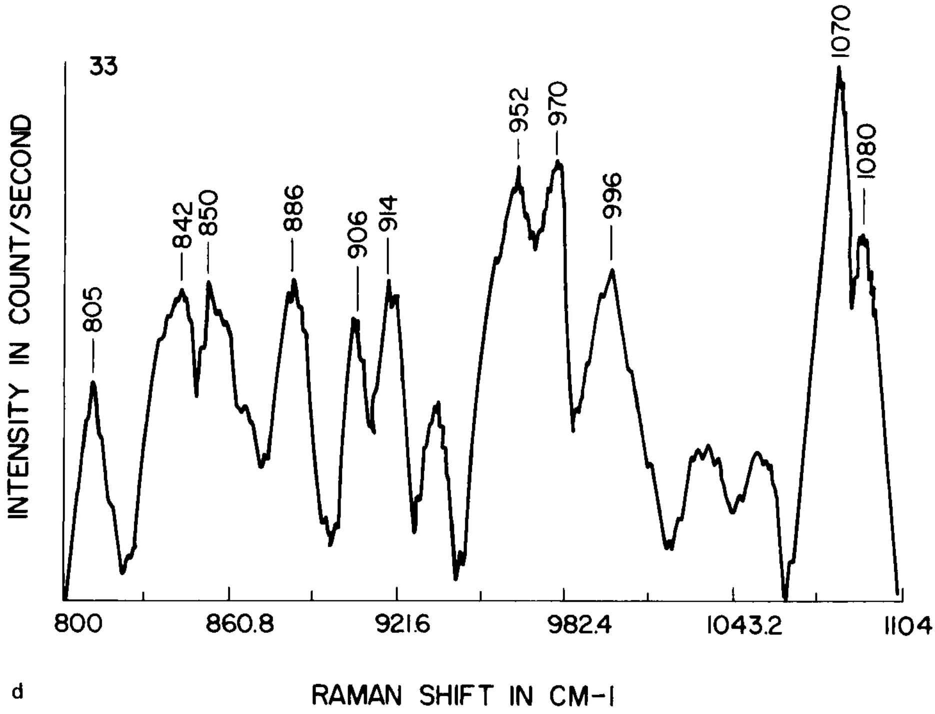

Fig. 1d

Dylewski *et al* (10) attributed the 1035 cm^{-1} Raman band to Si-O stretching in SiO$_2$. Yadav *et al* (11) reported that upon annealing the sample at 900°C, the Si-O stretching shifted to 1060 cm^{-1}. In our study the 1070 cm^{-1} above mentioned band not only represents the Si-O stretching vibration, but also suggests the possibility of some annealing during the ion bombardment process. Shapiro *et al* (12) reported a weak Raman shift in SiO$_2$ spectrum at 147 cm^{-1}, we are observing a band at 147 cm^{-1} with a shoulder on the low frequency side and our 198 cm^{-1} band could be the equivalent of the 207 cm^{-1} band of Shapiro *et al*, (but it is not a weak band). Pfeifter *et al* (13) have reported the possibility of a

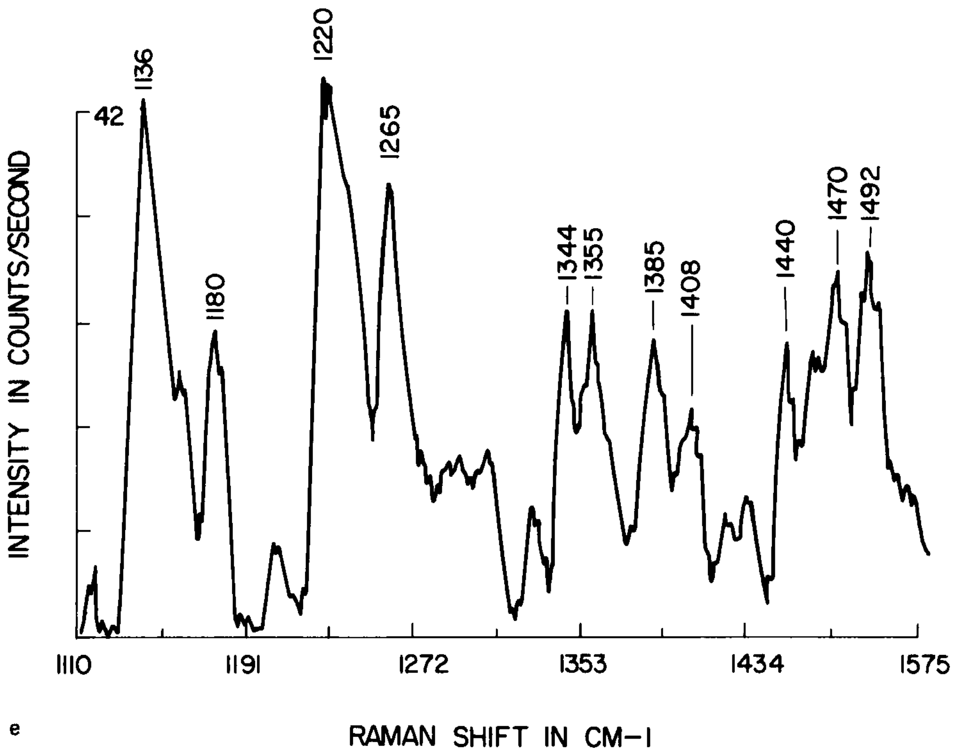

Fig. 1e

Fig. 1 (a-e) Raman spectrum of the D_2^+ implanted surface of P-type silicon. Entrance slit = 20μm, intermediate slit = 100μm and exit slit = 250μm.

a. 70-264 cm^{-1}, 30 mw laser power, 20 sec/step.

b. 270-499 cm^{-1}, 500 mw laser power, 5 sec/step.

c. 485-801 cm^{-1}, 500 mw laser power, 5 sec/step.

d. 800-1104 cm^{-1}, 500 mw laser power, 5 sec/step.

e. 1110-1515 cm^{-1}, 500 mw laser power, 5 sec/step.

Dark noise during the 5 sec/step is of the order of 9 counts and during the 20 sec/step is of the order of 36 counts/sec. Only those signals significantly higher than this dark noise level are being considered as real.

twisting vibration in SiO_2 at 115 cm^{-1}, corresponding band in our observations appear at 116 cm^{-1}.

Hastie et al (14) reported three bands at 850, 766 and 79 cm^{-1} in the Raman spectrum of SiO. We are observing bands at 855, 765 and 76 cm^{-1}, thus supporting the possibility of the existence of SiO complex on the surface of the silicon wafer. It was also pointed out by Hastie et al (14) that the 79 cm^{-1} broader dimer band might possibly be caused by the overlapping of two different frequencies. Our spectrum reveals two weak bands in this region, one being at 76 cm^{-1} as mentioned above and the other at 87 cm^{-1}.

Some hydrogen is present in deuterium as an impurity and it is likely that some H_2^+ will also be produced which in turn will interact with silicon to form some silicon-hydrogen complexes. One such possibility is Si_4H_4 which have been investigated earlier (15) and 906, 898, 658 and 637 cm^{-1} Raman bands have been observed. We are observing two equivalent Raman bands at 906 and 886 cm^{-1}, the remaining two bands, it appears, are overlapped by bands which will be discussed later. The possibility of the formation of Si_2H_6 is exhibited by the presence of Si-Si stretching mode at 434 cm^{-1} and SiH_3 bending mode at 914 cm^{-1}. These bands have also been observed by Gutowsky et al (16) in the Raman spectra of Si_2H_6 at 434.5 and 910-935 cm^{-1} respectively. Lucovsky (17) observed a Raman band at 842 cm^{-1} and assigned it to the $(SiH_2)_n$ wagging mode. We are also observing this band at 842 cm^{-1}, indicating the presence of $(SiH_2)_n$ type of complex on the surface of our sample. SiH_3 was found to have a IR active mode in the neighbourhood of 1000 cm^{-1} (18), our 996 cm^{-1} Raman band appears to be the equivalent. The 1244 cm^{-1} weak Raman (18) band (asymmetrical component of the 1220 cm^{-1} band) of Si_2H_6 appears as a weak Raman band at 1258 cm^{-1} in our spectrum.

The Raman spectra of Si_2H_6 as reported by Bethke et al (18) contains bands at 1490.7, 1446.6, 1364.3, 1139.0, 956.1, 833.3, 667.0, 683.1, 559.4, 474.7, 407.5, and 352.8 cm^{-1}. Our observations contain equivalent bands at 1492, 1440, 1358, 1136, 952, 850, 705, 674, 563, 474, 415, and 358 cm^{-1}, thus suggesting the formation of Si_2D_6 during bombardment of silicon with energetic D_2^+. The Si_2D_6 molecules thus formed get adsorbed on to the silicon surface and reveal their characteristic vibrations in the Raman spectrum of the D_2^+ implanted silicon surface. In addition the 1408 and 1346 cm^{-1} bands in our study are the overtones of the 705 and 674 cm^{-1} Raman bands mentioned above. Bethke et al (18) also observed a band at 277 cm^{-1} in the infrared spectrum of gaseous Si_2D_6 which was assigned as the XY_3 unsymmetrical rocking mode. This band was not observed in the Raman spectrum of the liquid Si_2D_6 (18). May be it was too close to the 4358 Å mercury line. We are observing a well defined Raman band at 262 cm^{-1}, which could very well be the equivalent band. The possibility of the formation of Si_4D_4 is evidence by the presence of the 454, 652, and 640 cm^{-1} Raman bands which have been reported earlier (15) at 454, 650 and 639 cm^{-1} in addition to the 490 cm^{-1} band which might be overlapped by the broad 488 cm^{-1} Raman band of a-Si in our observations.

Presence of several additional bands in our spectrum points towards the possibility of the formation of some other complexes. The relatively weak 1180 cm^{-1} Raman band in our spectrum has been reported by Lord et al (19) at 1180.4 cm^{-1} in the Raman spectrum of B_2H_6, thus suggesting the possibility of some B_2H_6 being formed on the surface. Boron here is the P-type impurity in silicon. Interaction of boron, the P-type impurity with the impinging ions to produce boron, hydrogen, etc. complexes has also been reported earlier (1,2). Formation of B_2H_6 is further evidenced by the presence of 588 and 1269 cm^{-1} bands which have been observed earlier (19) at 592 and 1270 cm^{-1} in the Raman spectrum of B_2H_6. Lehmann _et_ _al_ (20) reported a band at 260 cm^{-1} in the Raman spectrum of B_2D_5H and attributed it to $\delta(XY_{2b})$, we are observing a Raman band at 238 cm^{-1} suggesting the possible formation of a complex of the Type B_2D_5H also.

CONCLUSION

Our observations of the Raman spectrum of the D_2^+ implanted silicon surface, with a certain possibility of H_2^+, suggest the formation of not only a-Si layer on the crystalline surface but various other complexes involving Si, deuterium, hydrogen as well as boron, the P-type impurity in silicon. Some of these complexes might be highly reactive, still a small quantity can stay adsorbed on the surface, and reveal its characteristic vibrations in the Raman spectrum of the surface. Characteristics involving silicon and oxygen are also observed, since any exposure of silicon to atmosphere results in the formation of silicon oxides. The bands characterizing the boron, deuterium and hydrogen complexes are relatively weak, as can be expected, but nonetheless they are detectable, and their detection complements the sensitivity of the Surface Raman technique.

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