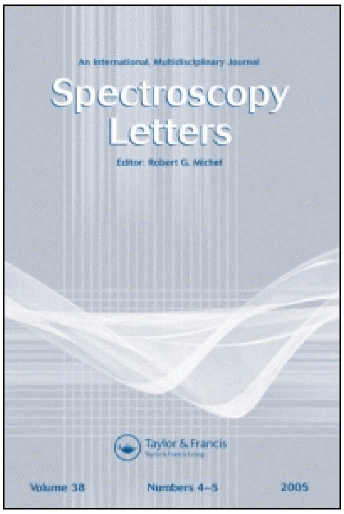

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Raman Scattering from $^{14}N_2$ and H_2 Bombarded Silicon Surface

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RAMAN SCATTERING FROM $^{14}N_2^+$ and H_2^+ BOMBARDED SILICON SURFACE

KEY WORDS: Raman Scattering from implanted silicon

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ABSTRACT:- The surface of a P type Si wafer was bombarded with $^{14}N_2^+$ and H_2^+ and the Raman spectrum of the implanted surface was obtained. The recorded spectrum not only confirms the information of various silicon-nitrogen, silicon-hydrogen, silicon-hydrogen-nitrogen-oxygen complexes but enables the identification of others.

INTRODUCTION

The process of ion implantation involves ionizing and accelerating atoms and causing them to enter a suitable material. Soon after penetrating the target material the energetic ion initiates a cascade of atomic collisions, sometimes very near the surface region, resulting in the formation of surface alloys of graded composition. Novel surfaces with interesting physical properties can thus be created by the technique of ion implantation. One such surface layer of silicon nitride is widely used as a passivating and dielectric thin film in semiconductor technology, and can be synthesized easily by the N_2^+

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bombardment of silicon surface. It has been shown by Smith _et al_ (1), Crowder _et al_ (2) and Bourgoin _et al_ (3) that the bombardment of crystalline silicon by a heavy dosage of ions ($\approx 10^{15}$ ions/cm^2) results in the formation of a continuous layer of amorphous silicon on the crystalline surface. The dangling bonds of the amorphous silicon layer can be passivated by bonded hydrogen. Metal-nitride-oxide-semiconductor films have memory applications and the presence of hydrogen also effects its characteristics . We are interested in the Raman characteristics of the surface formed by N_2^+ as well as H_2^+ implantation of a P-type silicon surface. Being complementary to the IR data, this Raman study of the implanted silicon surface, as mentioned above, is important to fully establish the structures formed on the surface of silicon by the implantation of both N_2^+ and H_2^+.

EXPERIMENTAL

A P-type single-crystal <111> cut Si wafer properly cleaned, etched and polished has been bombarded with ions produced in a linear accelerator* employing duo-plasmatron ion source. Dry CP-grade Nitrogen and Hydrogen gases are used as ion-source feed-in material and 30 keV $^{14}N_2^+$ and H_2^+ are implanted in the material. The total fluence is of the order of 10^{18} ions/cm^2. A liquid nitrogen cooled jacket is used around the target to prevent the deposition of pump oil vapours and to help achieve a good vacuum ($\approx 10^{-7}$ mm Hg).

The surface Raman facility at the University of Kentucky, Lexington (KY) USA, specifically designed to study the surfaces and surface Raman enhancements has been used to study the Raman characteristics of the implanted silicon surface. A sample wafer was mounted in an evacuated

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

chamber and the 5145 Å line of Ar^+ laser was allowed to illuminate a small portion of the implanted area through a high pressure window. Using a standard 90° geometry for Raman scattering, scattered radiation was collected by a specially designed optical collection system, and a cylindrical lens was used to transfer the Raman scattered radiation through another high pressure window on to the entrance slit of a Jarrell-Ash double monochromator. The monochromator was driven by a Burleigh-Piezo-electric Inchworm. The entire operation of the monochromator and the data acquisition by a photon counting technique is computer controlled. Average dark noise of the cooled photomultiplier during the 5 sec/step was of the order of 9 counts. The data was stored on a disc and was transferred to a plotter for display as required. Signals significantly higher than the background mentioned earlier were taken as real.

RESULTS AND DISCUSSION

As demonstrated earlier (1-3), the ion bombardment of crystalline surfaces by a heavy dosage ($\geq 10^{15}$ ions/cm^2) results in the formation of a continuous layer of amorphous silicon on the crystalline surface. Raman scattering from such a combination of crystalline and amorphous silicon should contain both amorphous and crystalline characteristics. Bourgoin _et al_ (3) confirmed this by simultaneous observation of a crystalline peak at 522 cm^{-1} as well as a-Si peak at 480 cm^{-1} in the Raman spectrum. In our observations the presence of both 520 and 488 cm^{-1} Raman peaks confirm the existence of a-Si layer on crystalline silicon surface. This combination of crystalline and amorphous silicon has been subjected to both $^{14}N_2^+$ and H_2^+ bombardment, resulting in the implantation of these ions in both types of silicon, which in turn is expected to result in the formation of various complexes involving Nitrogen, Hydrogen and amorphous as well as crystalline silicon. Exposure of silicon to atmosphere results in the formation of a SiO_2 layer on the silicon surface, which should also be revealed in the Raman spectrum. Komarov et al (4) have shown that the irradiation of silicon crystal with N_2^+ dosage in excess of 10^{17} ions/cm^2 results in the formation of non-stoichiometric complexes like Si_xN_y along with the precipitates of the phase Si_3N_4. Some of the characteristic activities of these complexes will be Raman active, and should be identifiable in the surface Raman spectrum of such a system. The Raman bands observed in our study of H_2^+ and N_2^+ implanted silicon are collected in Table 1 and are compared with the published IR and Raman data on silicon nitrogen and silicon hydrogen complexes. The Raman spectra of the N_2^+ and H_2^+ implanted crystalline silicon surface as recorded by us are displayed in Figures 1(a-g). Smith et al (1) 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. Our 305 cm^{-1} Raman band and the 305 cm^{-1} IR absorption in α-Si_3N_4 as observed by Komarov et al (4) are equivalent to the above 300 cm^{-1} Raman band (see Table 1). The Raman bands at 612 and 970 cm^{-1} are the overtones of the 305 and 488 cm^{-1} Raman bands discussed above, and following Brodsky et al (5) can be labelled as ω_{2LA} and ω_{2TO}. Following the earlier observations of Dylewski et al (6), the 802 and 1035 cm^{-1} Raman bands can be attributed to Si-O and Si-N stretchings in SiO_2 and Si_3N_4. Yadav et al (7) reported that upon annealing the implanted sample at 900°C, the Si-O and Si-N stretchings shifted to 1060 and 830 cm^{-1}. In our study Raman bands at 1070 (doublet) and 836 cm^{-1} are observed, suggesting the possibility of some annealing by the ion beam during bombardment. The 836 cm^{-1}

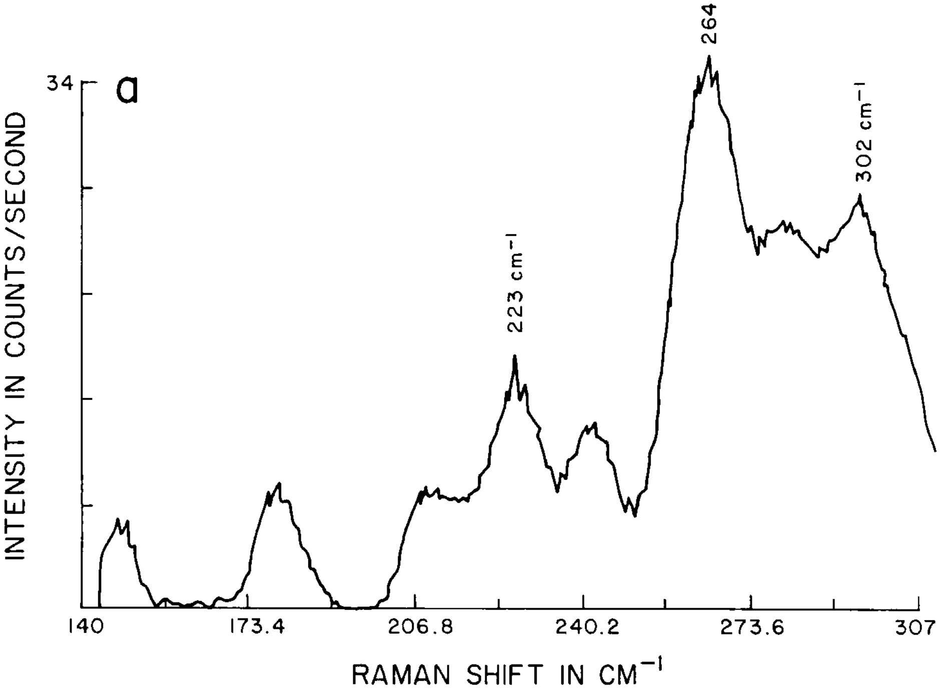
a
34
INTENSITY IN COUNTS/SECOND
RAMAN SHIFT IN CM^{-1}
140
173.4
206.8
240.2
273.6
307
223 cm^{-1}
264
302 cm^{-1}

Fig. 1a

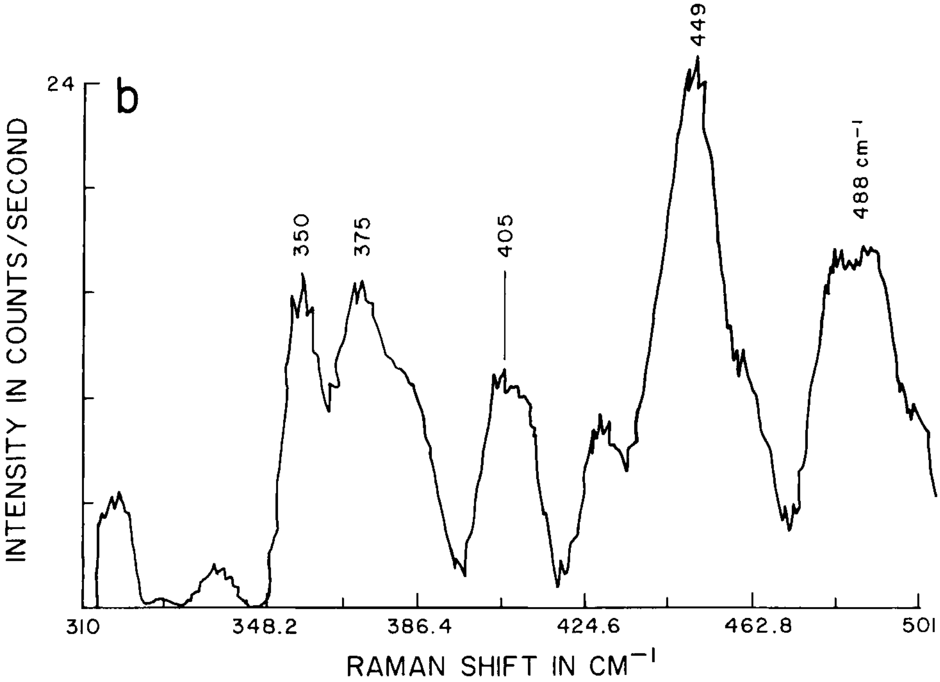
b
24
INTENSITY IN COUNTS/SECOND
RAMAN SHIFT IN CM^{-1}
310
348.2
386.4
424.6
462.8
501
350
375
405
449
488 cm^{-1}

Fig. 1b

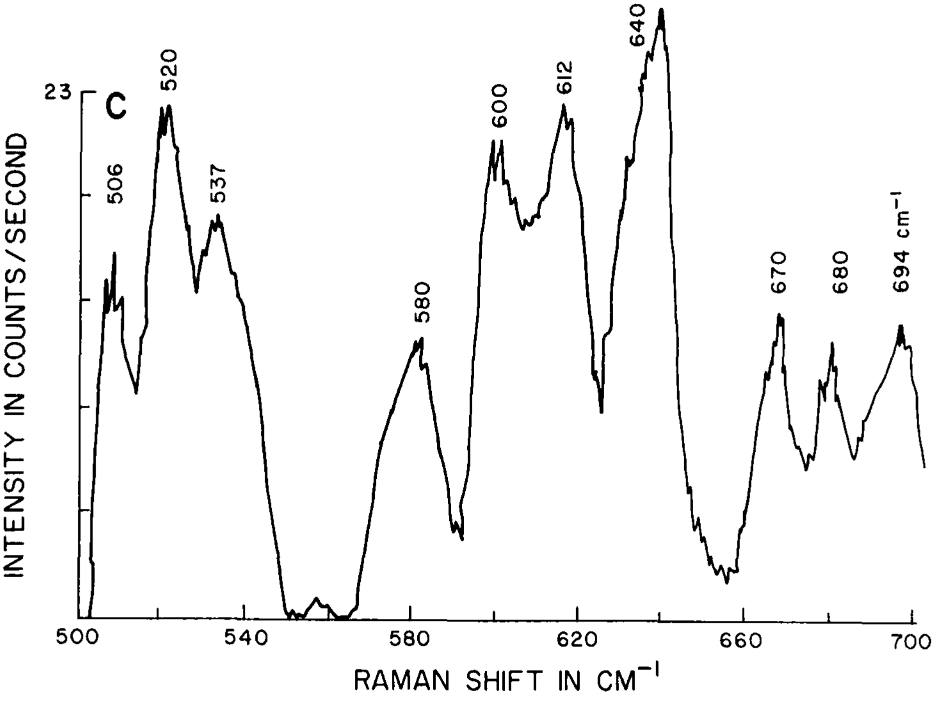

Fig. 1c

Raman band in our observation has a shoulder at 842 cm^{-1} which could be due to $(SiH_2)_n$ wagging mode (8). Brodsky et al (5) observed a Raman band at 380 cm^{-1} (shoulder), and assigned it to ω_{LO} or the longitudinal optical structure in a-Si. We also observe a doublet at 360-375 cm^{-1} which corresponds well with the 352 and 375 cm^{-1} IR absorptions of α-Si_3N_4 (4), and the 375 cm^{-1} Raman band can be attributed to ω_{LO}. Raman bands at 719 and 760 cm^{-1} are overtones of the 352 and 375 cm^{-1} Raman bands above. Hass (9) 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 the atoms

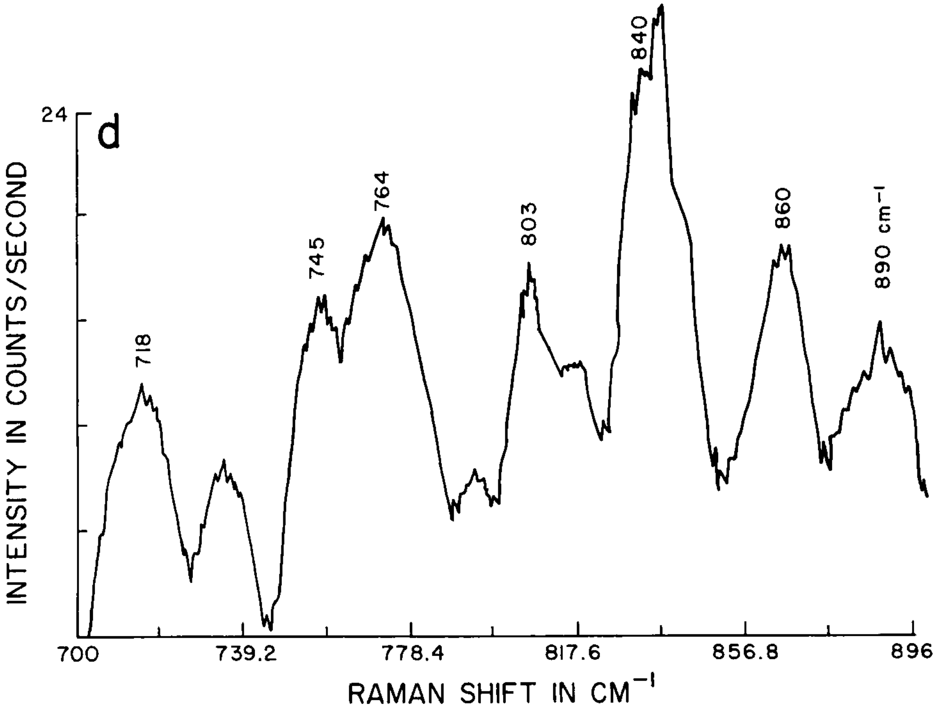

Fig. 1d

move roughly perpendicular to the Si-O-Si planes, and has its equivalent in our study at 445 cm^{-1}. The 800 cm^{-1} Raman band in SiO_2 spectrum of Hass, as mentioned above, has been associated with the 'bond-bending' type of motion in which the oxygen moves approximately at 90° to Si-Si lines in Si-O-Si planes. This mode was calculated by Lippincott et al (10) to be at 730 cm^{-1}. In our study this band appears at 803 cm^{-1}. The bond-stretching vibrations in SiO_2 in which the bridging oxygens move in opposite directions to their Si neighbours, and roughly parallel to the Si-Si lines was assigned by Hass (9) to the 1067 cm^{-1} Raman band. In our study the 1080 cm^{-1} component of the 1070 cm^{-1} doublet discussed earlier; could be the equivalent 'bond-stretching' vibration. Hass also

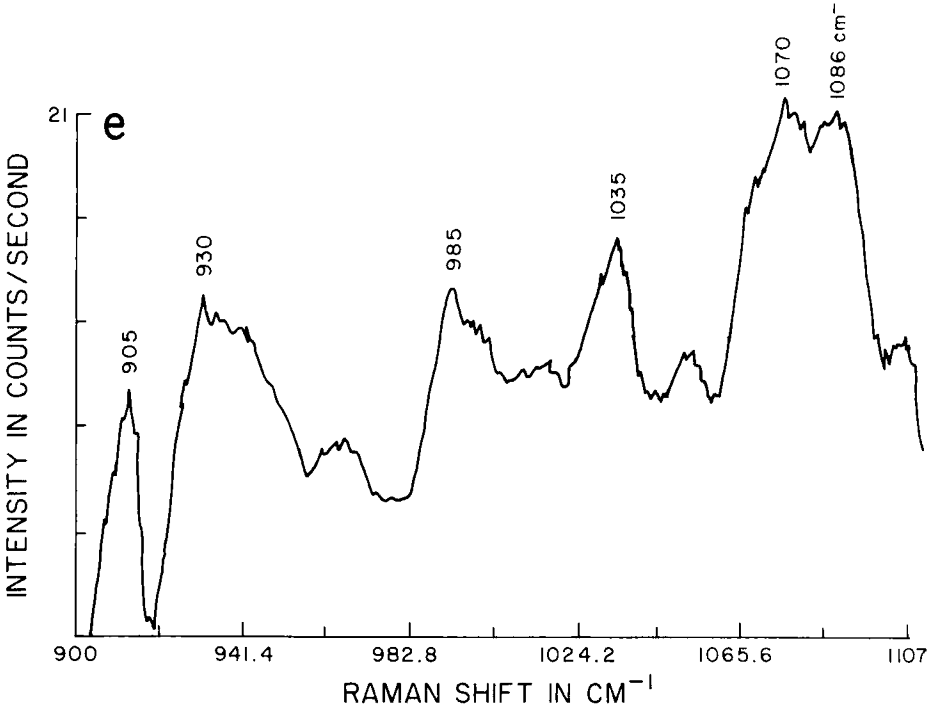
e
21
INTENSITY IN COUNTS/SECOND
905
930
985
1035
1070
1086 cm⁻¹
900
941.4
982.8
1024.2
1065.6
1107
RAMAN SHIFT IN CM⁻¹

Fig. 1e

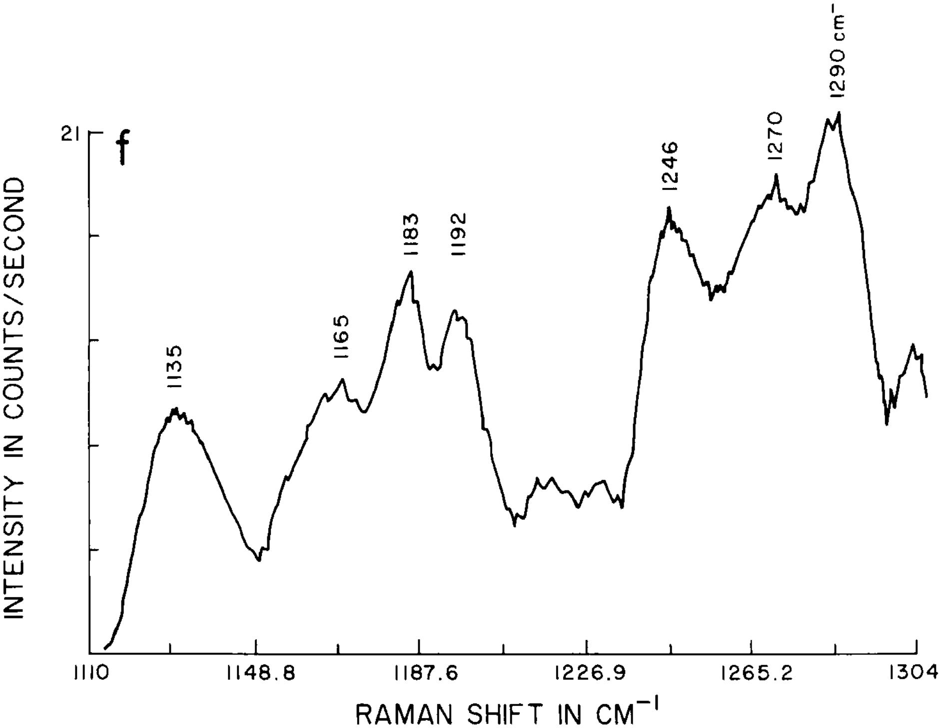
f
21
INTENSITY IN COUNTS/SECOND
1135
1165
1183
1192
1246
1270
1290 cm⁻¹
1110
1148.8
1187.6
1226.9
1265.2
1304
RAMAN SHIFT IN CM⁻¹

Fig. 1f

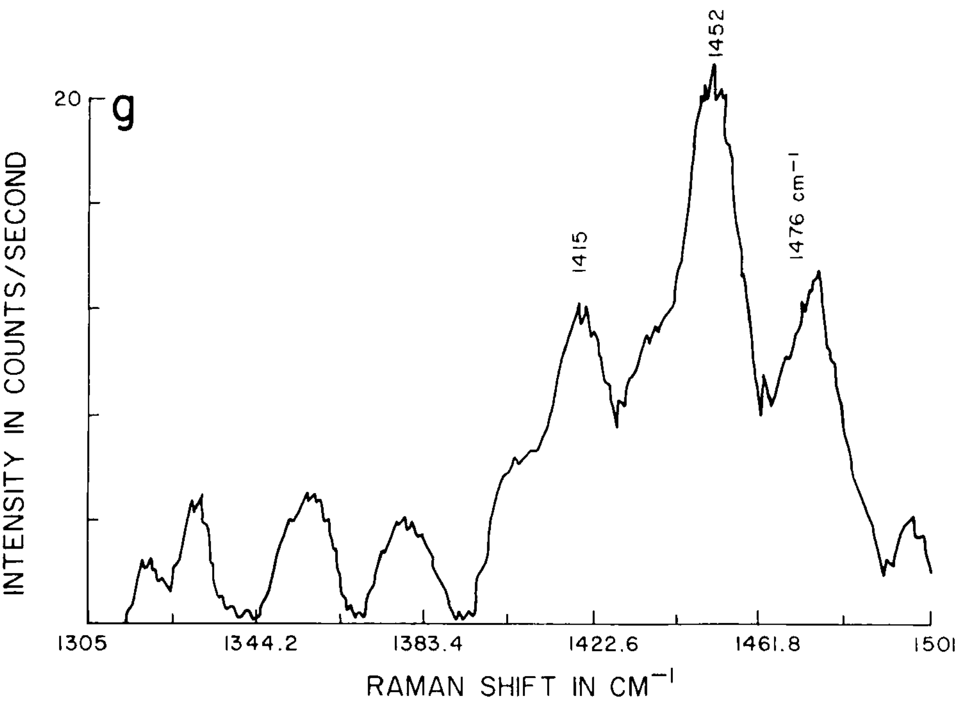

Fig. 1g

Fig. 1 (a-g) Raman spectrum of the $^{14}N_2^+$ and H_2^+ implanted surface of P-type silicon. Entrance slit = 250μ intermediate slit = 100μ, and exit slit = 250μ with 5 sec/step and 1 Watt laser power. a) 140-307 cm^{-1} region b) 310-501 cm^{-1} region c) 500-700 cm^{-1} region d) 700-896 cm^{-1} region e) 900-1107 cm^{-1} region f) 1110-1304 cm^{-1} region g) 1305-1501 cm^{-1} region. Dark noise during the 5 sec/step is of the order of 9 counts. Only those signals significantly higher than this dark noise here are being considered as real.

Table 1. IR Absorption and Raman Bands of N^+ and H^+ implanted Si

(a)	(b)	(c)	(d)	(e)	(f)	(g)
Si_3N_4	α-Si_3N_4	β-Si_3N_4	SiH	SiO_2	SiO_2	$^{14}N_2^+ + H_2^+$ imp.Si
IR (cm^{-1})	IR (cm^{-1})	IR (cm^{-1})	IR (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	Raman (cm^{-1})
						223
						264
	305		300			305
355	352					350
370	375	376	380 (Sh)			375
405	403				410 (S)	405
432		445		443 (S)		449
460		461				
485	493	496	480		490 (S)	488
	501					506
	510					520
		537				537
570					568 (W)	580
					600 (W)	600
	605		610			612
	660		660			640
	668					670
	676	680				680
	684					694
						718
	750					745

(continued)

Table 1 (continued)

						764
				811 (M)	800 (W)	803
862	858		845			840
						860
885	896		890			890
906		906				905
927						930
	985	980				985
1030	1045	1040				1035
				1061		1070
						1086
						1135
						1165
						1183
				1200		1192
						1246
						1270
						1290
						1415
						1452
			1460			1476

a) Komarov et al (4) b) Volgin et al (11) c) Miller (15) d) Hass (9)
e) Knights et al (12) f) our data on the surface Raman of $^{14}N_2^+$, H_2^+ implanted P-type Si.
S = strong, M = medium, W = weak, Sh = Shoulder

observed bands at 490 and 600 cm^{-1}, which were not assigned. The 600 cm^{-1} Raman band above appears at 600 cm^{-1} in our study also, and the 490 cm^{-1} band has been assigned and discussed earlier. The 1200 cm^{-1} Raman band of SiO_2 as observed by Hass (9) has its equivalent in our spectrum at 1192 cm^{-1}.

The Si_3N_4 spectra in the infrared region of 1200 to 200 cm^{-1} as observed by Komarov et al (4) indicates strong absorptions at 927, 885 and 847 cm^{-1}. Our Raman spectrum contains equivalent bands at 930, 890, and 861 cm^{-1}. The Si_3N_4 IR spectra as reported by Komarov et al (4) contains a band at 1030 cm^{-1}, which was reported by Volgin et al (11) as an IR absorption at 1045 cm^{-1} for (α-Si_3N_4) and at 1040 cm^{-1} for (β-Si_3N_4). Our Raman spectra contains a corresponding band at 1038 cm^{-1}.

Knights et al (12) reported the IR and Raman spectra of a-Silicon-hydrogen alloys with reference to Si_4H, Si_3H_2, Si_2H_2 where upon, one, two and three hydrogen atoms respectively are bonded to silicon atom which in turn is bonded to silicon network. The hydrogen atoms thus act as termination of what otherwise would be dangling bonds. Knights et al (12) discussed the presence of the 650 cm^{-1} band as due to a Si-H stretching mode due to hydrogen bonded singly to the silicon atom. We are observing a Raman band at 640 cm^{-1} which very well could be the band discussed above. Knights et al (12) also discussed that a combination of SiH_2 and SiH_3 groups will produce modes in the 800-950 cm^{-1} region and predicted (by the use of four body forces) that both SiH_2 and SiH_3 clusters can exhibit a mode at 900 cm^{-1}. Our 905 cm^{-1} Raman band could very well be that predicted above. The 506 and 537 cm^{-1} Raman bands in our study find their equivalent in the IR studies of Volgin et al (11) at 510 and 537 cm^{-1} assigned to ν_4 (F_2), N-Si-N bending vibrations in α-Si_3N_4 and β-Si_3N_4. The 1287 cm^{-1} Raman band in our study is an overtone of the 642 cm^{-1} band discussed earlier. Gruen et al (13) have reported a Si-H stretching vibration at 1460 cm^{-1}, and our 1452 cm^{-1} Raman band is in direct correspondence with it.

A band at 1180.4 cm^{-1} has been reported by Anderson et al (14) in the spectrum of B_2H_6. The presence of a 1183 cm^{-1} band in our spectrum suggests the possibility of the formation of B_2H_6 in the implanted P-type silicon with boron being the P-type impurity. Miller et al (15) have reported the IR spectrum of BN^- and observed a strong absorption at 1380 cm^{-1}. In our study a shoulder appears at 1395 cm^{-1}, which very well could be the equivalent. These bands are relatively week, but they are definitely observable. The concentration of boron in silicon as a P-type impurity is in the ratio of 1 to 10^3. The possibility of the impinging ion beams interacting with the relatively small concentration of boron atoms is very real. The small concentration of the boron complexes as Raman scatterers, will yield very weak Raman signals, which under normal circumstances would be difficult to resolve from the background. But the high resolution of the equipment used in the present study enables the detection of these boron complexes through their characteristic vibrations.

The possibility of the formation of other complexes is evidenced by the presence of some Raman bands, which have not been reported earlier. These additional bands appear at 1130, 1165, 1246, 1270 and 1476 cm^{-1}. We have mentioned the possibility of the formation of B_2H_6 as characterized by the presence of 1180.4 cm^{-1} band. BH_3 on the other hand has a characteristic Raman mode at 1125 cm^{-1} (16), the presence of a 1130 cm^{-1} Raman band in our observations again supports the possibility of the interaction of H^+ with boron, the P-type impurity to produce few BH_3

molecules on the surface of the crystalline silicon. Another possibility can be the mutual interaction of N^+ and H^+ on the surface to form some complexes which are adsorbed on the surface. This is evidenced by the presence of 1165 and 1270 cm^{-1} Raman bands which are very close to the N-N-N symmetric stretch-bending and bending-symmetric stretching mode of N_3H reported by Pimentel et al (17) to be at 1168 and 1273 cm^{-1} respectively. The 1246 cm^{-1} Raman band in our observation might be the equivalent of the 1224 cm^{-1} IR absorption band of SiO_2 as reported by Anderson et al (18). The presence of the 1476 cm^{-1} Raman band provides strong evidence for the formation of planar N_2H_2 complex, which has been reported to exhibit N = N stretching at 1481 cm^{-1} (19). Some of the observed bands, for example the 305, 375, 405, 488, 803 and 840 cm^{-1} bands are within few cm^{-1} of the bands of various complexes as reported in Table 1. This may be the reason why these bands are relatively broad. We are observing an envelope covering the various components too closely to be resolved.

CONCLUSION

The bombardment of P-type silicon with ${}^{14}N_2^+$ and H_2^+ not only results in the formation of an amorphous silicon layer but in various complexes involving silicon, nitrogen, hydrogen and boron, the P-type impurity. Any exposure of silicon to air results in the formation of a layer of silicon oxide, and thus oxygen also gets into the picture. In fact a complex ensemble of crystalline and polycrystalline silicon along with a host of complexes mentioned above has been subjected to Raman investigation, hence the larger number of Raman peaks. The simultaneous presence of SiO_2, SiO, Si_3N_4 and SiH supports the synthesis of a hydrogenated silicon oxinitride layer of the type $(Si_xO_yN_z)\ H_W$. Complexes of the type B_2H_6, BH_3, BN^-, N_3H, SiO, SiO_2 in addition to both α and β type

Si_3N_4 and SiH have been detected in the Raman spectrums of the surface of $^{14}N_2^+$ and H_2^+ implanted P-type silicon. In addition the synthesis of N_3H and N_2H_2 has also been demonstrated. The sensitivity of the Raman technique is well established by the present results.

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