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Surface Chemistry of Hydrogen-Passivated Porous Silicon

-Oxidation of Surface Si-H Groups by Acetone

by

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Submitted To

Langmuir

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Abstract

The oxidation of hydrogen-passivated porous silicon by acetone at room temperature has been observed by using transmission infrared spectroscopy. After reaction with liquid acetone, two infrared absorption modes at 2253 cm^{-1} and 2200 cm^{-1} develop, and this is accompanied by loss of absorbance of the Si-H stretch modes at 2142 cm^{-1} , 2110 cm^{-1} and 2089 cm^{-1} . We postulate that oxidation of the surface silicon hydride species by acetone to form $(\text{CH}_3)_2\text{HCO-Si-H}_x$ and $[(\text{CH}_3)_2\text{HCO}]_2\text{-Si-H}_x$ species has occurred. This surface reaction may be utilized for passivation of the silicon surface.

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I. Introduction

It has recently been discovered that porous silicon formed by electrochemical etching of silicon in HF + C₂H₅OH photoluminesces in the visible when excited by ultraviolet light [1]. The discovery has initiated interest in the physical structure of the porous silicon and in the mechanisms responsible for the photoluminescence [1-12]. The porous silicon is characterized with silicon microstructures a few nanometers wide but microns in length, and a huge inner surface area of 200-300 m²/cm³ [1, 5]. The prepared silicon surface contains a high coverage of chemisorbed hydrogen [6-8]. It is believed that the hydrogen termination passivates the dangling bonds at the surface of the small silicon crystallites [1, 8]. Arguments have been made that surface silicon hydride species play a key role in the photoluminescence of porous silicon [3, 4, 7, 11]. The photoluminescence effect is strongly attenuated by a number of polar adsorbates on the porous silicon surface [4], suggesting that surface species are important in governing the process.

There are a few reports on the effects of surface chemical reactions on the structure of porous silicon. It has been found that some strong oxidants such as HNO₃ or H₂O₂ oxidize the porous silicon as reported by Nakajima et al. [9].

Acetone is a very common organic solvent being used to rinse porous silicon [10]. It is also used as a solvent for the preparation of porous silicon [11, 12]. Therefore, it is important to understand the surface reactions of acetone with hydrogen-terminated porous silicon. We report here the interaction between acetone and the silicon hydrides of porous silicon. So far, there are no reports concerned with the reaction of acetone with surface silicon hydrides on porous silicon, single crystal silicon, or amorphous silicon.

II. Experimental

The porous silicon samples we used in our experiments were made from boron doped p-type Si(111) single crystals, 10 ohm-cm resistivity. The sample holder for the electrochemical etch of the Si is made of Teflon. We anodized the silicon wafer in an electrolyte consisting of a 1:1 mixture of 48% aqueous HF and 95% ethyl alcohol. A constant current density of 16.3 mA/cm^2 for 2 minutes was employed. The total charge flow through the sample was 1.2 C. After the anodized silicon was air dried, its infrared spectrum was measured. We then immersed the porous silicon in liquid acetone for 5 minutes at room temperature, and after drying measured the IR spectrum again. We then put the wafers into 48% HF (aqueous) and after drying measured the IR spectrum once again. In contrast to studies by others [9], we found that the acetone reaction and HF rinse could be carried out without physically detaching the porous silicon film from the silicon substrate.

We measured the transmission IR spectra using a Mattson Research Model FTIR instrument at a resolution of 2 cm^{-1} . The instrument was equipped with a KBr beam splitter and a liquid-nitrogen cooled HgCdTe detector. The instrument optical compartment and sample compartment were purged with dry nitrogen gas. Impurity hydrocarbon species present on the silicon prevent IR studies in the CH_3 stretching and deformation regions at present.

III. Results

Figure 1 exhibits the transmission IR spectra in the Si-H stretching frequency region, showing the effect of the acetone reaction and the successive HF rinse. Figure 1(a) is the IR spectrum of the as-anodized porous silicon wafer. The presence of Si-H_x stretch modes at $2150\text{-}2050 \text{ cm}^{-1}$ is consistent with previous observations that porous silicon is produced with a hydrogen-terminated surface [6-8]. The Si-H_x

absorption frequencies and line shapes are similar to samples luminescing in the red/infrared (750nm) as reported by Collins et al.[7, 8]. By comparison with those features obtained by the multiple internal reflection IR spectroscopic technique for HF-etched Si(111) and Si(100) surfaces as reported by Chabal et al.[13], we assign the 2142, 2110 and 2089 cm^{-1} bands to the Si-H stretch modes of SiH_3 , SiH_2 and Si-H species, where overlap of various modes of the three species contribute to the three broad features shown in Fig. 1.

The anodized silicon wafer was immersed in acetone (Mallinckrodt, spectra AR) for 5 minutes. Then the silicon wafer was taken out of the liquid acetone, dried in air and transferred into the IR spectrometer's sample compartment. The IR spectrum of this sample is shown in Figure 1(b). As shown clearly in the difference spectrum (b)-(a) in Figure 2, the striking differences between the before- and the after-acetone reaction are the appearance of the two intense and broad bands (shaded) at 2253 cm^{-1} and 2200 cm^{-1} , and the decrease in the intensity of the original tri- di- and mono-hydride stretching bands (unshaded) at 2142, 2110 and 2089 cm^{-1} .

In Figure 1c the IR spectrum of the porous silicon is shown after successive rinses with 48% HF (aqueous) for 5 minutes. The spectrum is qualitatively the same as that of the as-anodized porous silicon before reaction with acetone. But, the intensities of the Si-H modes are now smaller. As shown in the difference spectrum of Figure 2 (c)-(b), the high frequency Si-H modes, which appear after the acetone reaction, then disappear after the HF rinse(shaded). This indicates that the surface species responsible for the two high frequency SiH_x modes have been chemically removed by the HF (aqueous) treatment.

IV. Discussion

It has been well established that oxidation of hydrogen-covered porous silicon [10, 14], polysilanes [15], and hydrogenated amorphous silicon [16] results in a blue-shift of the Si-H stretch frequencies. Higher loading with oxygen atoms results in higher frequency Si-H modes [16]. For instance, Gupta et al. [14] have observed two higher frequency bands at 2268 cm^{-1} and 2176 cm^{-1} after heating partially hydrogen-covered porous silicon at 600 K in O_2 (g). They assigned the two bands to the Si-H stretching modes of Si-H species backbonded to three and two oxygen atoms, respectively. Fully oxidized polysilane $(\text{SiH})_x$ exhibits strong absorbance at 2260 cm^{-1} for $(\text{O}_3\text{SiH})_x$; oxidation of $(\text{SiH}_2)_x$ results in IR bands at 2190 cm^{-1} for $(\text{OSiH}_2)_x$ and 2245 cm^{-1} for $(\text{O}_2\text{SiH}_2)_x$ [15].

In view of these earlier studies, we conclude that the surface silicon hydride species are oxidized upon reaction with acetone. We assign the band at 2253 cm^{-1} to an Si-H stretching mode of Si-H_x species in which the silicon atom is bonded to 2 or 3 oxygen atoms. The 2200 cm^{-1} band may be due to a Si-H stretching mode of Si-H_x species that are bonded to one oxygen atom less than the species giving the 2253 cm^{-1} band.

In the lower frequency region, we note that broad features at 1250 cm^{-1} , 1074 cm^{-1} and $880\text{-}836\text{ cm}^{-1}$ develop after the acetone reaction (not shown). They disappear along with the oxidized Si-H stretching bands at 2253 cm^{-1} and 2200 cm^{-1} after the HF rinse. We tentatively assign the 1074 cm^{-1} band to the Si-O-C asymmetric stretching modes of the Si-O-C by comparison to the IR absorption modes of $(\text{CH}_3)_3\text{SiOCH}_3$ (Si-O-C asymmetric stretch at 1083 cm^{-1} and symmetric stretch at 865 cm^{-1}) [17].

Air oxidation of porous silicon is very slow at room temperature. In a separate

experiment the oxidation of porous silicon was not observed by IR after 3 hours exposure of the as-anodized porous silicon to air. This is in agreement with previous reports by Kato et al. [6]. They have studied air oxidation of porous silicon at 406 - 606 K and have found that only 17% of the SiH species are oxidized after the porous silicon has been heated in air at 406 K for 100 minutes. Therefore, the oxidant for the faster oxidation of surface silicon hydrides observed here at ~ 300 K was not air, but acetone. This has been confirmed by subsequent experiments under vacuum using acetone vapor and oxygen gas [18].

Alkylsilanes (R_3SiH , R_2SiH_2 and $RSiH_3$) have been recognized as useful reducing agents for the stereo controlled reduction of organic carbonyl compounds such as ketones, aldehydes and esters in organic/pharmaceutical chiral synthesis chemistry [19-22]. In the presence of fluoride ions [20, 21], the reaction is catalyzed and for ketones produces silyl ethers ($R_2CHOSiR_xH_{3-x}$) in high yields of 80-100% at 273 K. The porous silicon being made in HF (aqueous) solution contains F atoms on its surface as revealed clearly by XPS studies [12]. The atomic ratio of Si:F for the first 2.5 nm surface was about 50:12 [12].

By analogy to the well-established organic reaction process, we propose that the reduction of acetone carbonyl groups by surface silicon hydrides occurs when porous silicon is reacted with liquid acetone at room temperature. Thus, the carbonyl group is an oxidizing agent for $Si-H_x$ surface species. As shown in Figure 3, the carbonyl group of the acetone attacks the Si atom of SiH_x species, forming an associated complex $(CH_3)_2CO: \rightarrow Si-H_x$. The formation of the complex

$(CH_3)_2CO: \rightarrow SiH_3(C_6H_5)$ between phenylsilane ($C_6H_5-SiH_3$) and acetone in liquid phase has been observed by H-NMR and IR spectroscopies [23]. In the complex, the Si-H bond is weakened and this facilitates a subsequent hydrogenation reaction to give

the silyl ether products $(\text{CH}_3)_2\text{HCO-Si-H}_{x-1}$). For the SiH_2 and SiH_3 surface species, secondary and tertiary reactions probably also occur, and may produce oxidized surface species such as $[(\text{CH}_3)_2\text{CHO-}]_2\text{-Si}$, $[(\text{CH}_3)_2\text{CHO-}]_2\text{-SiH}$ and $[(\text{CH}_3)_2\text{CHO-}]_3\text{-Si}$. The presence of surface F atoms may accelerate the reaction as was found in the organic synthesis [20, 21].

As a result of this surface oxidation process, most of the properties of porous silicon, luminescence included, change with the acetone reaction. Moreover, successive rinses with HF (aqueous) solution remove the oxidized silicon hydride species from the Si substrate. Hence, both the amount of the surface silicon hydride species decreases and the structure of the porous silicon layer changes as a result of the reaction of surface SiH_x groups with acetone. The extent of the oxidation depends on the duration of the acetone reaction. Whether the acetone reaction affects the photoluminescence of porous silicon will be interesting to study in connection with the photoluminescence mechanism.

It is likely that other ketones, $\text{RR}'\text{CO}$, and aldehydes, RCHO , will oxidize SiH_x groups on silicon surfaces. By changing the alkyl R groups of the ketones or aldehydes, controlled modification and passivation of silicon surfaces can be achieved.

V. Summary

We have found that acetone is an oxidizing agent for surface SiH_x groups on porous silicon. Based on infrared observations, surface moieties such as $(\text{CH}_3)_2\text{HCO-Si-H}_{x-1}$ are postulated to be formed as Si-H bonds are broken by reaction with the carbonyl group.

VI. Acknowledgment

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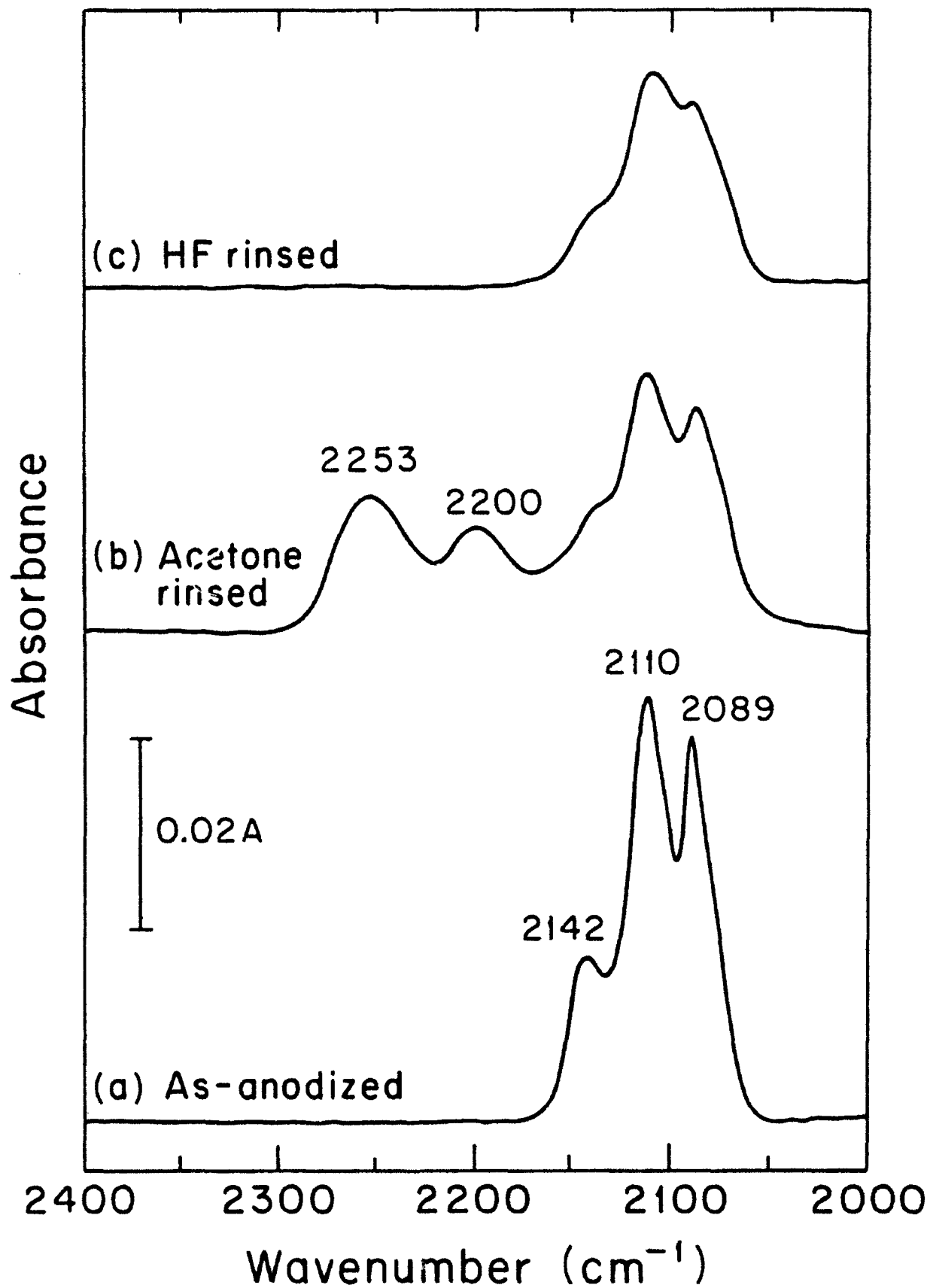
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Figure 1. FTIR spectra of porous silicon. (a) as-anodized; (b) reacted with acetone at room temperature for 5 min; (c) successively rinsed with HF (aqueous).

Figure 2. Difference spectra of (b)-(a) and (c)-(b). The IR spectra shown in Fig. 1 of porous silicon are: (a) as-anodized; (b) reacted with acetone at room temperature for 5 min; and (c) successively rinsed with HF (aq), respectively.

Figure 3. Proposed reaction between acetone and silicon hydride species on porous silicon at 300 K.

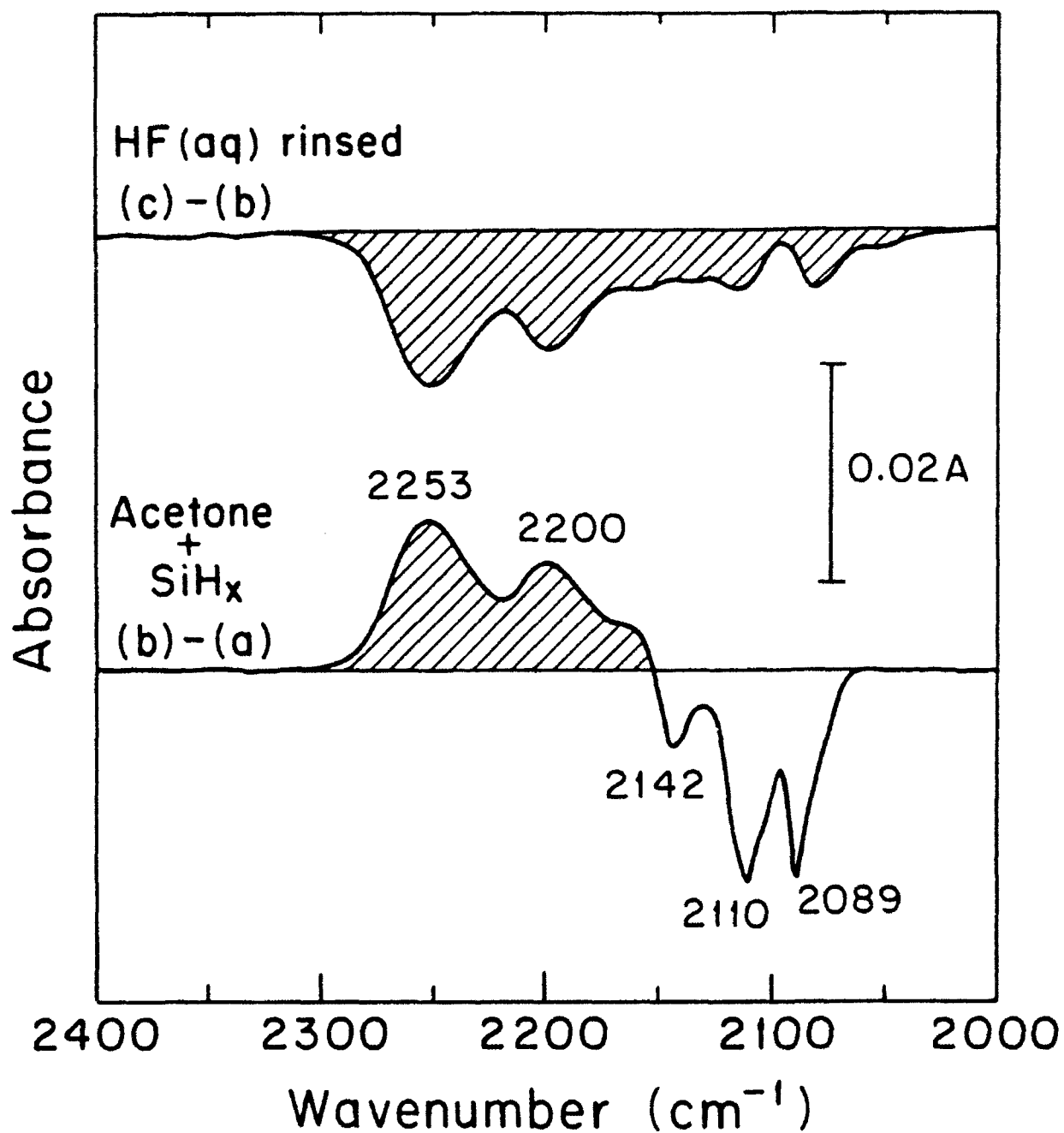
Interaction of Si-H_x with Acetone



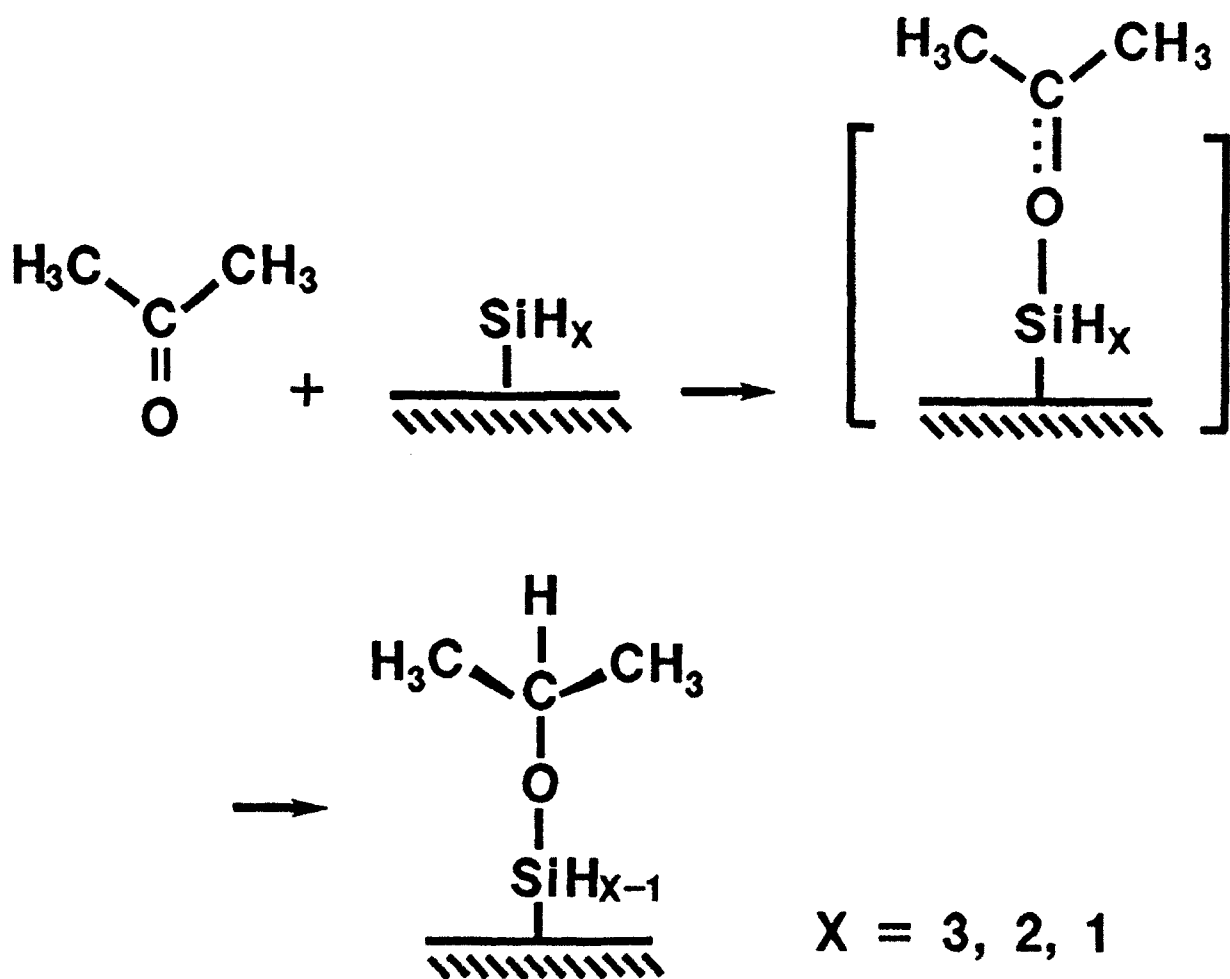
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Figure 1

Effect of Acetone and HF (aq) on Si-H_x Modes - Difference Spectra



Proposed Reaction between Acetone and Silicon Hydrides on Porous Silicon at 300 K



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