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The Role of Backbond Strain in Silicon Surfaces on the Decomposition of NH_3 and PH_3

by

M.L. Colaianni, P.J. Chen and J.T. Yates, Jr.

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Abstract

Silicon adatoms on the $\text{Si}(111)-(7\times 7)$ surface form strained Si-Si backbonds with underlying silicon atoms. The strain at adatom sites causes both $\text{NH}_2(\text{a})$ and $\text{PH}_2(\text{a})$ to be thermally unstable compared to the same species on the $\text{Si}(100)-(2\times 1)$ surfaces which contains less-strained silicon surface atoms. The surface strain induces enhanced $\text{NH}_2(\text{a})$ and $\text{PH}_2(\text{a})$ dissociation on $\text{Si}(111)-(7\times 7)$ adatom sites compared to $\text{Si}(100)-(2\times 1)$. Thus both $\text{NH}_2(\text{a})$ and $\text{PH}_2(\text{a})$ can participate in recombination reactions on $\text{Si}(100)$ to produce major amounts of $\text{NH}_3(\text{g})$ and $\text{PH}_3(\text{g})$ above 600 K; such reactions are absent on $\text{Si}(111)-(7\times 7)$ surfaces.

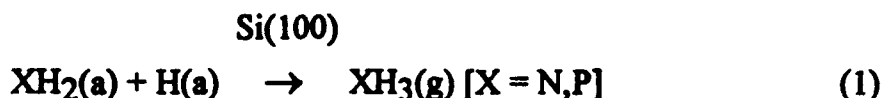
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The behavior of chemisorbed species on silicon single crystals is expected to be influenced by the crystal structure of the surface. In this report, two group V hydrides, NH_3 and PH_3 , have been compared on $\text{Si}(100)-(2\times 1)$ and $\text{Si}(111)-(7\times 7)$ surfaces, and we report an important common phenomenon governing the mechanism of thermal decomposition of these chemisorbed molecules. The Si-Si backbond strain effect on $\text{Si}(111)$ is found to govern adsorbate decomposition. This concept may also apply to other semiconductor surfaces and could be significant in governing semiconductor doping and a wide variety of thin film formation processes.

On both $\text{Si}(100)$ and $\text{Si}(111)$ surfaces, NH_3 and PH_3 molecules adsorb dissociatively at ~ 100 K to produce $\text{NH}_2(\text{a})$ [1-6] and $\text{PH}_2(\text{a})$ [7-10] species. These species have been detected by vibrational spectroscopic methods. In addition, at higher surface coverages, undissociated $\text{NH}_3(\text{a})$ and $\text{PH}_3(\text{a})$ molecules are also populated. On $\text{Si}(111)-(7\times 7)$, both $\text{NH}_2(\text{a})$ and $\text{PH}_2(\text{a})$ species decompose at higher temperatures, eventually producing chemisorbed $\text{N}(\text{a})$ and $\text{P}(\text{a})$ along with desorbing $\text{H}_2(\text{g})$ [1,2,7,8,10]. In contrast, on $\text{Si}(100)-(2\times 1)$, a major recombination process, kinetically competitive to dissociation, occurs at about 500 - 600 K [1,3,4,8], as shown by equation 1.



This recombination process reduces the effectiveness of Si(100) to produce N(a) or P(a) species from XH₃ compared to Si(111).

Figure 1 shows a comparison of the NH₃ and PH₃ temperature programmed desorption from both (100) and (111) silicon surfaces. Both surfaces weakly bond some NH₃ or PH₃, and desorption of these molecular adsorbates occurs below 300 - 500 K. However, for Si(100)-(2x1) in the temperature range 600 - 700 K, the evolution of additional XH₃(g) is also observed (cross hatched). XH₃ is not evolved from Si(111)-(7x7) in this temperature range as shown in Figure 1. In the case of both NH₂ and PH₂ adsorbed on Si(100)-(2x1) containing some adsorbed D(a), recombined XH₂D(g) is the major species produced in the 600 - 700 K range [3,4,8]. This confirms that the surface recombination process shown in equation 1 occurs on Si(100)-(2x1) but not on Si(111)-(7x7). For NH₂(a) on Si(100), we estimate that about 73% of the nitrogen from NH₂(a) is evolved according to equation 1 [1].

The question therefore is why XH₂(a) species participate in recombination reactions on Si(100)-(2x1) but not on Si(111)-(7x7). This difference in surface behavior of XH₂(a) species on the two silicon surfaces is postulated to be due to the special nature of Si adatom surface sites on Si(111)-(7x7). These sites cause the facile decomposition of adsorbed XH₂(a) species, and this decomposition reaction competes effectively with the XH₂(a) + H(a) recombination reaction process shown in equation (1).

Figure 2 shows the two major types of Si sites on Si(111)-(7x7) - an adatom site containing $\text{XH}_2(\text{a})$ [$\text{X}=\text{N};\text{P}$] and a restatom site. In addition, $\text{XH}_2(\text{a})$ on Si(100)-(2x1) is shown. The adatom site involves considerable Si backbond strain (4 member Si ring structures beneath the adatom), whereas less backbond strain is present at the rest atom site (6 member Si rings) [11,12], or on Si(100). The backbond strain effect at the Si adatom site is postulated to cause X-H bond scission in $\text{XH}_2(\text{a})$, followed by the insertion of the X-H species into the broken backbond as shown in Figure 2. This results in the thermal instability of the XH_2 species on a Si adatom site compared to XH_2 on a Si rest atom site or on a Si_2 dimer site on Si(100)-(2x1), both of which sites involve less strain [11-13]. Vibrational spectroscopic studies for $\text{NH}_2(\text{a})$ on Si(111)-(7x7) identify the production of $\text{NH}(\text{a}) + \text{H}(\text{a})$ and indicate that $\text{NH}_2(\text{a})$ is thermally unstable [~ 600 K decomposition] compared to $\text{NH}_2(\text{a})$ on Si(100)-(2x1) [>600 K decomposition]. A similar relative instability is observed for $\text{PH}_2(\text{a})$ on Si(111) compared to Si(100), as seen by vibrational spectroscopy [7,8]. Thus, it is the thermal instability of $\text{XH}_2(\text{a})$ species on Si(111) adatom sites which leads to the absence of the recombination process to produce $\text{XH}_3(\text{g})$.

Similar effects of backbond strain are likely to occur for many semiconductor-adsorbate systems, as has already been reported for example for hydrogen etching of Si(111)-(7x7) [14,15]. Thus, chemistry at the surface of covalent solids can be profoundly influenced by local bond strain effects at the dangling bond sites.

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Figure Captions

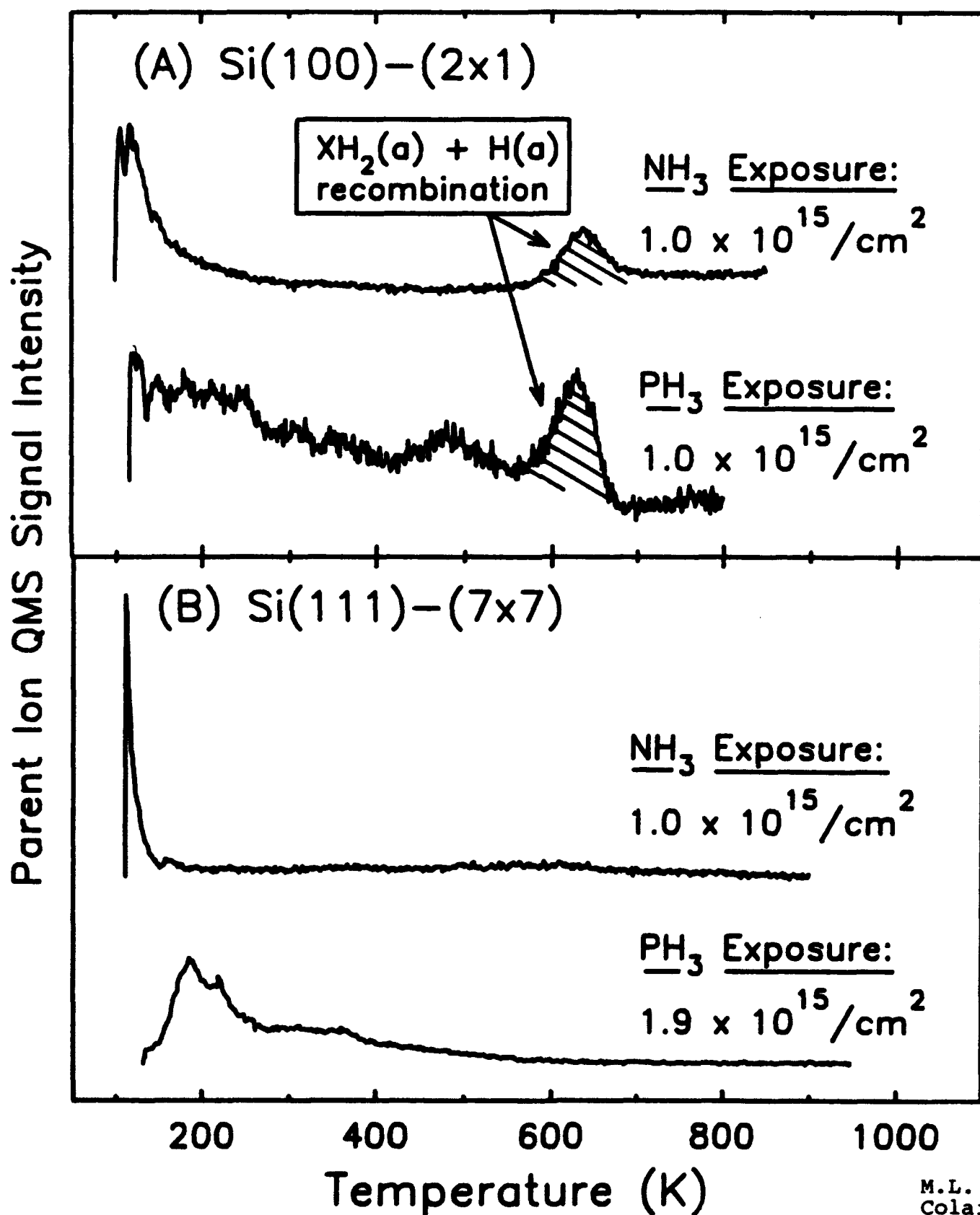
Figure 1. Temperature programmed desorption spectra showing that $\text{XH}_2(\text{a}) + \text{H}(\text{a}) \rightarrow \text{XH}_3(\text{g})$ recombination processes occur for NH_3 and PH_3 on the $\text{Si}(100)\text{--}(2\times 1)$ surface (A), but are absent on the $\text{Si}(111)\text{--}(7\times 7)$ surface (B). The heating rates employed were 1 K/s for the ammonia desorption spectra, 1.6 K/s for PH_3 desorption from $\text{Si}(111)\text{--}(7\times 7)$ and 2.0 K/s for PH_3 desorption from $\text{Si}(100)\text{--}(2\times 1)$.

Figure 2. Schematic representation showing various bonding sites on the $\text{Si}(111)\text{--}(7\times 7)$ and $\text{Si}(100)\text{--}(2\times 1)$ surfaces. Also shown is the dissociation pathway which is proposed to occur on the $\text{Si}(111)\text{--}(7\times 7)$ surface - XH_2 decomposition accompanied by the rupture of the strained adatom backbond, followed by insertion of the -NH or -PH species.

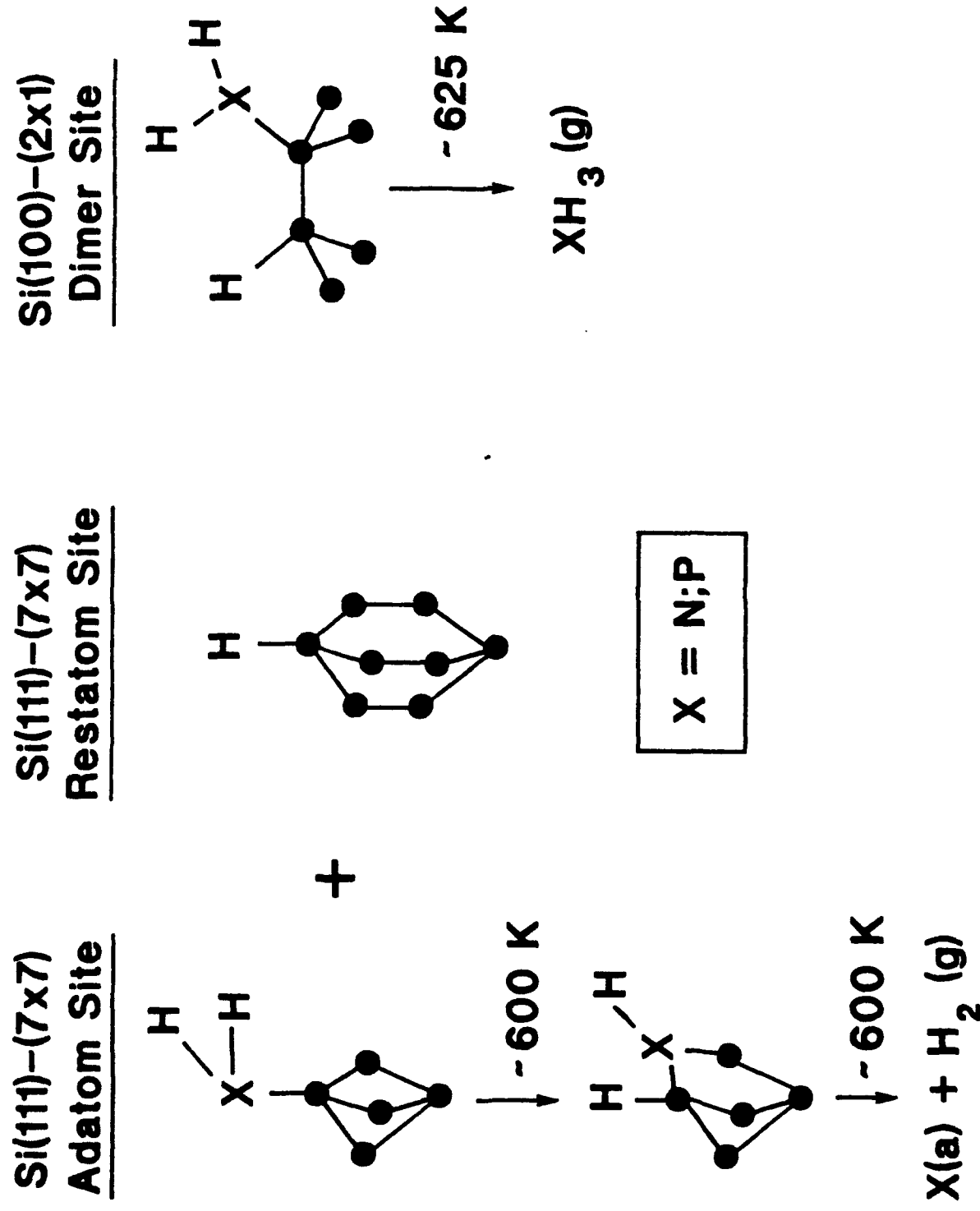
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Comparison of the Thermal Desorption of NH_3 and PH_3 from $\text{Si}(100)-(2 \times 1)$ vs. $\text{Si}(111)-(7 \times 7)$



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