In situ Infrared Evidence for the Electrochemical Incorporation of Hydrogen into Si and Ge

K. C. Mandal
University of South Carolina - Columbia, mandalk@engr.sc.edu

F. Ozanam

J.-N. Chazalviel

Follow this and additional works at: https://scholarcommons.sc.edu/elct_facpub

Part of the Electrical and Electronics Commons, and the Other Chemistry Commons

Publication Info
© Applied Physics Letters 1990, American Institute of Physics
http://dx.doi.org/10.1063/1.103788
http://scitation.aip.org/content/aip/journal/apl/57/26/10.1063/1.103788

This Article is brought to you by the Electrical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.
In situ infrared evidence for the electrochemical incorporation of hydrogen into Si and Ge
K. C. Mandal, F. Ozanam, and J.-N. Chazalviel

Citation: Applied Physics Letters 57, 2788 (1990); doi: 10.1063/1.103788
View online: http://dx.doi.org/10.1063/1.103788
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/57/26?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Si/Si Ge n-type resonant tunneling diodes fabricated using in situ hydrogen cleaning

Evidence for atomic H insertion into strained Si–Si bonds in the amorphous hydrogenated silicon subsurface from in situ infrared spectroscopy

Evidence for hydrogen incorporation during porous silicon formation

Experimental evidence for a kinetic model of hydrogen incorporation into sputtered a-Si films
AIP Conf. Proc. 73, 20 (1981); 10.1063/1.33079

Infrared Evidence for the Existence of Hydrogen Bonds
J. Chem. Phys. 4, 749 (1936); 10.1063/1.1749785
In situ infrared evidence for the electrochemical incorporation of hydrogen into Si and Ge

K. C. Mandal, F. Ozanam, and J.-N. Chazalviel
Laboratoire de Physique de la Matière Condensée, ²Ecole Polytechnique, 91128 Palaiseau, France

(Received 19 July 1990; accepted for publication 19 October 1990)

The electrochemical incorporation of hydrogen into n-Si and n-Ge has been studied by Fourier-transform electrochemically modulated infrared spectroscopy. Fresh (111) silicon (resp., germanium) surfaces exhibit a vibrational band at 2080 (resp., 1960) cm⁻¹ corresponding to a surface Si--H (resp., Ge--H) bond perpendicular to the surface. Prolonged cathodic treatment results in a new band at 2000 (resp., 1900) cm⁻¹. The position and polarization dependence of this band indicate that it is associated with hydrogen inside the semiconductor lattice. These observations directly show for the first time that cathodically hydrogenated samples contain a thin, disordered, and highly hydrogenated layer, which is probably responsible for the improvement of the hydrogen evolution kinetics observed on these electrodes.

Recently there has been considerable interest in the role of hydrogen in amorphous or crystalline semiconductors. This is mainly due to the ability of hydrogen for passivating dangling bonds, and neutralizing various defects in Si and Ge as well as other semiconductors. There are various ways of introducing hydrogen into semiconductors, such as ion implantation, growing crystals in H₂ atmosphere, glow discharge in hydrogen, or in hydrogen-producing ambient. Electrochemical incorporation of hydrogen has also been used. In all cases, it is difficult to obtain chemical or structural information about the nature of hydrogen present in the solid by only electrical techniques. Infrared (IR) spectroscopy has already been found to be useful for getting this kind of information. Here we have used Fourier-transform electrochemically modulated infrared spectroscopy (FTEMIRS) for investigating the early stages of H incorporation into Si and Ge during electrochemical loading. Modulation of the electrode potential provides a unique way for extracting the weak IR absorption of the interface from the much larger electrolyte absorption background.

Hydrogen incorporation was carried out electrochemically at room temperature in a 0.5 M H₂SO₄ electrolyte in a three-electrode cell. Si and Ge single crystals were used as the working electrode, a Pt wire as the counter electrode, and a Hg/Hg₂SO₄ electrode as the reference. From now on, all the potentials are referred to this reference. The n-type Si and Ge samples were cut from (111) oriented ingots, both with a donor concentration N_d ≈ 2 × 10¹⁵ cm⁻³. The samples were used in a multiple-reflection geometry as reported elsewhere. The optical faces were lapped and polished successively by emery powder, zirconium oxide powder, and diamond paste of various grain sizes down to 0.25 μm. For the Si sample, the final polishing of the face to be exposed to the electrolyte was carried out mechanochemically for a few hours with a solution of Cu(NO₃)₂ and NH₄F, and for the Ge sample, the final polishing was done mechanochemically with an alkaline silica gel. The final etching of the samples was carried out by applying five to six times the following cycle: 40% HF dip, ultrapure water rinse, sulphochromic mixture dip, new water rinse, final drying by blowing pure nitrogen. Just before mounting the electrode against the cell, it was rinsed for 1 min in 40% HF; this procedure gave the best results as it removed the oxide from the surface. Before starting infrared measurements, pure nitrogen gas was bubbled through the electrolyte to remove any dissolved oxygen. The optical setup is a home-built Fourier-transform spectrometer for electromodulated IR spectroscopy and consists of a lanthanum-chromite IR source, a Michelson interferometer with a very slow scanning speed (6 μm s⁻¹), and a mercury-cadmium-telluride photovoltaic detector. The details of the experimental assembly and data acquisition can be found elsewhere. The experiments are controlled by an Olivetti M24 microcomputer via an IEEE 488 bus. The whole experimental setup is placed in a glove box with a positive pressure of purified dry air to remove CO₂ and H₂O vapor. We now present the experimental results, which will be discussed in the following sections.

The current potential characteristics of freshly prepared Si and Ge electrodes in 0.5 M H₂SO₄ electrolyte are shown in Fig. 1 [curves (a1), (b1), and (b2)]. A noteworthy feature of these curves is the appearance of a small voltammetric wave during the cathodic sweep. Like for metals, it may be attributed to the first step of hydrogen reaction preceding the gas evolution. This occurs at -1.1 V for Si and -1.0 V for Ge. Clearly, in both cases there is no reoxidation peak observed during the anodic cycle. Continuous potential cycling in the hydrogen evolution region (typically in the range -1.0 to -2.0 V for either Si or Ge) results in a significant shift of the onset of hydrogen evolution [see Fig. 1, curves (a2) and (b3)]. The shift amounts to ±0.3 V towards anodic potentials and appears progressively in ≈ 5 h. The same result can be

²Unité de Recherche 1254 associée au Centre National de la Recherche Scientifique.
reached upon keeping the electrode under 10–100 mA/cm² cathodic current density for the same duration.

Figure 2(a) shows the electromodulated spectra for silicon before prolonged cathodic treatment. The peak at 2080 cm⁻¹ is clearly similar to that found ex situ on the spectra of HF-rinsed silicon surfaces as well as in situ on that of the Si surface in contact with an HF electrolyte. This peak is then attributed to the stretching mode of a surface Si—H bond. After flowing a cathodic current through the electrode (100 mA/cm², 12 h) the vSiH band appears with a very different shape, and is now shifted to 2000 cm⁻¹ [see Fig. 2(b)]. This rather low frequency is reminiscent of the vSiH bands, which are observed in a-Si:H or of the prominent vSiH line at 1980 cm⁻¹, which has been assigned to the vibration of a (Si)₂SiH defect in crystalline silicon. This suggests that the observed signal may arise from hydrogen incorporated into the silicon lattice. Further support of this conjecture can be obtained from polarization studies. For brevity, we will show this only for the case of Ge.

The spectra for a freshly etched Ge surface in 0.5 M H₂SO₄ are shown in Fig. 3(a). The spectra for s and p polarization are separately shown. An important observation is that, for p polarization a strong vGeH signal appears at ~1500 cm⁻¹, whereas for s polarization its intensity is negligibly small. This observation is consistent with the picture of a Ge—H bond perpendicular to the surface. This corresponds with the naive expectation for a surface hydride species on the (111) face; the position of the band is also in close agreement with the literature. Figure 3(b) shows the spectrum obtained after modification of the electrode by cycling its potential between ~0.7 and ~1.2 V during 2 h. The vGeH band now appears broader and slightly shifted to lower energies. Also, a small contribution is now discernible for s polarization. The effect of further prolonged cathodic treatment is represented in Fig. 3(c). The band is now centered around 1900 cm⁻¹ and its intensity is approximately equal for s and p polarization. Also its width appears larger than that of Fig. 3(a).

Our data provide direct confirmation for penetration of H into the Si and Ge lattice. The fact that the s and p signals have equal magnitude for the cathodically treated surface is strong evidence that the associated species is lying inside the semiconductor. Indeed a surface species will equally absorb infrared radiation in s and p polarization only if it is strictly parallel to the surface but this
would occur in a very peculiar geometry of the surface which seems very unlikely here. Furthermore, the position of the observed bands is very comparable to that of vSiH (vGeH) in the solid.

Due to the electromodulation technique, we are probing a very thin layer (a few tens of nanometers). From the observed magnitude of the signal—which we have been unable to observe in standard transmission (difference) spectra—a rough estimate of $10^{15}$ cm$^{-2}$ Si--H (Ge--H) bonds may be inferred. This indicates that the concentration of H in this layer is very high ($\sim 10^{21}$ cm$^{-3}$). The broadness of the spectra shows that it is rather disordered.

The efficiency of the electrochemical loading of hydrogen into semiconductors has been demonstrated by secondary-ion mass spectroscopy profiling of D. In silicon, the profiles indeed exhibit a high concentration of D atoms near the surface. On the other hand, roughening of the silicon surface has been reported by several authors when silicon is maintained under cathodic conditions during several hours. We have also checked, in routine scanning electron microscopy verifications, that damaging appears at the surface of our electrodes after prolonged cathodic treatment. Our spectroscopic findings suggest a bridge between these various observations; they bring evidence for the presence of a thin disordered layer at the semiconductor surface, containing a high concentration of hydrogen. Damaging of the surface is clearly associated with this high density of incorporated hydrogen: massive penetration of hydrogen will induce a high density of lattice defects; also the H atoms will tend to form H$_2$ molecules, and the formed bubbles will tend to break the already weakened lattice.

This modification of the semiconductor surface is probably related to the change in the current potential curves. The anodic shift of the onset of H$_2$ evolution upon prolonged cathodic treatment has also been reported by others. However, the mechanism is not clear. We think that the enhancement of specific surface area due to surface roughening can hardly account for the observed improvement in hydrogen evolution kinetics. Rather, the breaking of the crystal lattice in the damaged layer will tend to enhance the density of active sites, thereby enhancing the capability of H adsorption and H$_2$ formation.

In conclusion, we bring the first direct evidence that electrochemical incorporation of H into Si and Ge takes place by formation of a thin disordered highly hydrogenated layer at the surface. The observed disorder directly arises from the incorporation of hydrogen into the lattice, and is not due to extraneous phenomena such as, e.g., ion bombardment in plasma treatments. This observation is consistent with the various pieces of data available in the literature.