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Low temperature removal of surface oxides and hydrocarbons from Ge(100) using atomic hydrogen

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Abstract

Germanium is a group IV semiconductor with many current and potential applications in the modern semiconductor industry. Key to expanding the use of Ge is a reliable method for the removal of surface contamination, including oxides which are naturally formed during the exposure of Ge thin films to atmospheric conditions. A process for achieving this task at lower temperatures would be highly advantageous, where the underlying device architecture will not diffuse through the Ge film while also avoiding electronic damage induced by ion irradiation. Atomic hydrogen cleaning (AHC) offers a low-temperature, damage-free alternative to the common ion bombardment and annealing (IBA) technique which is widely employed. In this work, we demonstrate with x-ray photoelectron spectroscopy (XPS) that the AHC method is effective in removing surface oxides and hydrocarbons, yielding an almost completely clean surface when the AHC is conducted at a temperature of 250 °C. We compare the post-AHC cleanliness and (2×1) low energy electron diffraction (LEED) pattern to that obtained via IBA, where the sample is annealed at 600 °C. We also demonstrate that the combination of a sample temperature of 250 °C and atomic H dosing is required to clean the surface. Lower temperatures prove less effective in removal of the oxide layer and hydrocarbons, whilst annealing in ultra-high vacuum conditions only removes weakly bound hydrocarbons. Finally, we examine the subsequent H-termination of an IBA-cleaned sample using XPS, LEED and ultraviolet photoelectron spectroscopy (UPS) in order to examine changes in the work function of Ge(100) upon hydrogenation.

Keywords: Germanium, atomic hydrogen cleaning, surface cleaning, x-ray photoelectron spectroscopy, low energy electron diffraction, ultraviolet photoelectron spectroscopy

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1. Introduction

Group IV semiconductor materials have received much attention over the past two decades, with applications in molecular electronics [1, 2] and semiconductor-on-insulator devices [3]. Whilst most of the current microelectronics industry is based on silicon, recent developments have led to the incorporation of other elements, or indeed a direct replacement of Si, in order to engineer properties such as improved resilience and the band gap of the material for improved or new device applications. In particular, germanium is currently employed in either elemental or alloy form in many areas, including optical devices [4–6], integrated circuits [7], wireless communications [8], solar cells for space probes [9], light-emitting diodes [10], production of polyethylene [11], tarnish-proof alloys [12], and single-crystal detectors in security systems [13]. In many of these applications, the ability to prepare a clean, ordered Ge surface, free from oxide contamination, would be particularly advantageous.

Traditional methods of surface preparation, such as argon ion bombardment and annealing (IBA), are known as an avenue to producing clean Ge(100) surfaces [14]. Typically the resulting surface exhibits a (2×1) asymmetric dimer reconstruction at room temperature in low energy electron diffraction (LEED) and scanning tunnelling microscopy (STM) [15–17]. However, this cleaning approach introduces considerable electronic damage in to the material, introducing defects, enhanced carrier concentrations and reduced mobility to the outermost approx. $1\mu\text{m}$ of the material. Similar work on Si surfaces has revealed the formation of amorphous layers within the Si structure [18]. Upon annealing these amorphous layers recrystallize epitaxially on the underlying Si, but leave residual dislocations and dipoles which adversely affect the electronic properties of the Si layer. At the surface, however, the atoms have more freedom to move around and the energy afforded by annealing at 600 C is sufficient to generate a well-ordered surface and high quality LEED pattern.

Clean Ge(100)- (2×1) surfaces have also been produced via ex-situ wet etching and annealing [19–21], and via plasma cleaning using either oxygen [22] or hydrogen [23]. The clean surfaces yielded by these preparation methods have been employed in several surface science studies, including the adsorption of isomers [24], multifunctional ketones [25] and water adsorption [26]. However, almost all of these studies involve an annealing stage in excess of 600 °C, something which is not desirable under circumstances where a clean surface is required and segregation or diffusion reduce the performance of the device.

Atomic hydrogen cleaning (AHC) has been shown to offer an effective route to the removal of surface hydrocarbons and oxides in a range of semiconductor materials, including GaP [27], GaMnAs [28], GaAs [29], GaSb [30], InAs [31, 32], InN [33], and InP [34]. The AHC process removes surface oxides and hydrocarbons via chemical reaction on the surface, followed by desorption in to the vacuum, and ordered surfaces can typically be achieved at lower temperatures. While AHC at room temperature can lead to the formation of a rough surface, various studies on semiconductor and metallic surfaces have shown that annealing at relatively low temperatures can remove a significant quantity of these defects [35–38]. It should be noted that the unreconstructed Ge(100) surface possesses dangling bonds. Both the formation of an asymmetric dimer reconstruction [14] and the chemisorption of H atoms leading to the formation of a Ge(100)- (2×1) :H surface are therefore possibilities with this cleaning method. In previous work this monohydride surface has been prepared via IBA, followed by a dose of atomic hydrogen [39], with a proposed work function shift of 0.2 eV with respect to the clean Ge(100)- (2×1) surface [40]. Hydrogen-terminated surfaces of Si, Ge and diamond have been shown to be chemically passive, relatively inert and have potential technological uses [41–43], which can then be functionalized for a wide range of applications [44].

In this article, we have employed x-ray photoelectron spectroscopy (XPS) and LEED to study the effectiveness of the AHC process at low substrate temperatures to remove native germanium oxides and atmospheric contamination from the Ge(100) surface, to leave behind a well-ordered Ge(100)- (2×1) surface reconstruction. We also employ LEED and ultra-violet photoelectron spectroscopy (UPS) to study the change in surface ordering and work function of a sample which is cleaned using IBA and subsequently H-terminated. This provides an insight in to the termination of the post-AHC surface.

2. Experimental Details

Previous work has shown that high-quality Ge layers can be grown directly on to clean Si(100) using reduced pressure chemical vapour deposition (RP-CVD) [45, 46]. In this work we use one such film, grown to a thickness of approximately $1\mu\text{m}$. The experiments detailed in this paper were performed at the Science City Photoemission

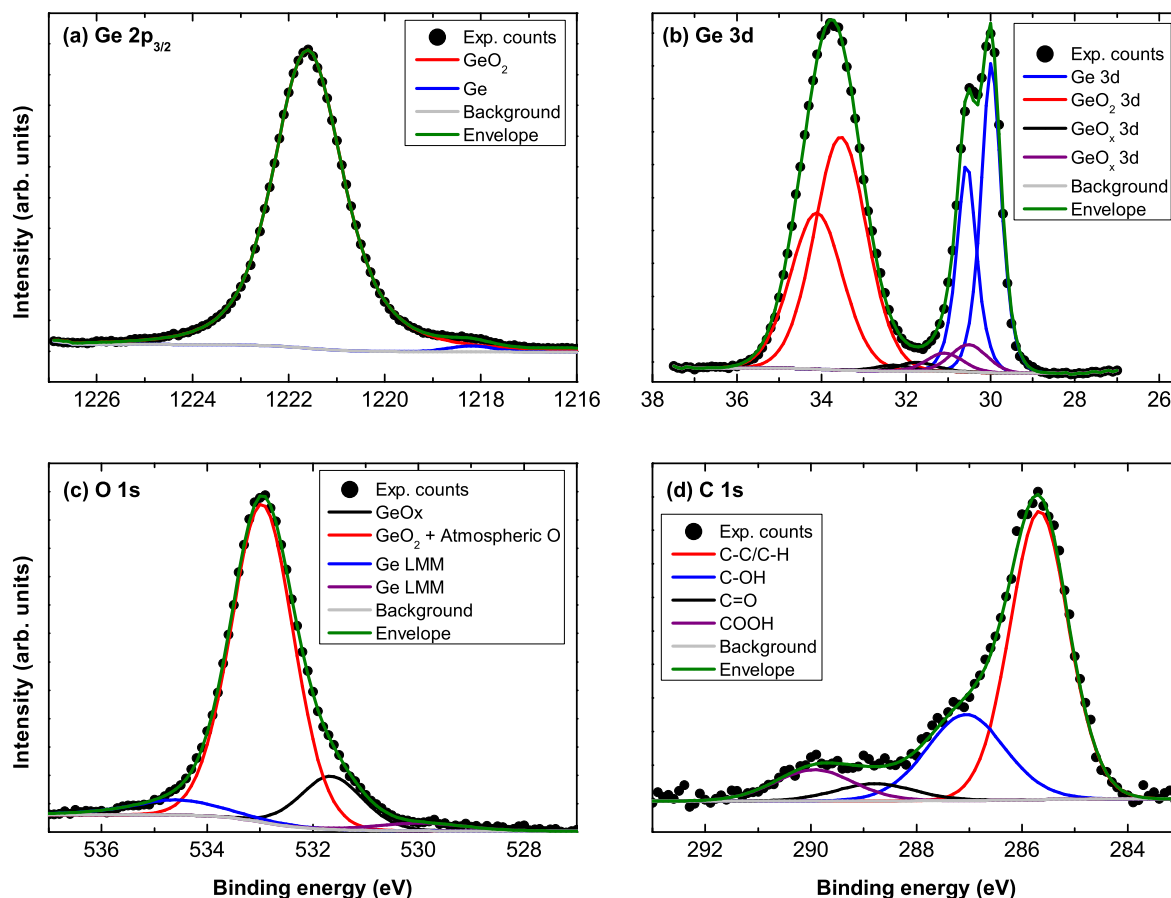


Figure 1. (Colour online) As-loaded core level XPS spectra from the Ge(100) surface prior to atomic hydrogen cleaning. The (a) Ge $2p_{3/2}$, (b) Ge $3d$, (c) O $1s$ and (d) C $1s$ regions all exhibit the Ge oxides and atmospheric contamination typically observed on semiconductor surfaces (peak assignments are described in the main text).

50 Facility at the University of Warwick [47]. The samples were mounted on to Omicron-style sample plates using Ta
 51 foil and loaded in to the fast-entry chamber. Once the fast-entry chamber had been evacuated, the samples were
 52 transferred to the 12-stage carousel for storage at pressures of less than 1×10^{-10} mbar. XPS and UPS data were
 53 acquired in the main analysis chamber using an Omicron SPHERA analyser (Omicron Nanotechnology, UK). Core
 54 level XPS spectra were recorded using a pass energy of 10 eV (0.47 eV resolution), with the sample illuminated using
 55 an Omicron XM1000 monochromated Al K_{α} x-ray source ($h\nu = 1486.6$ eV). Analysis of the XPS data was carried out
 56 using the CasaXPS software [48], using mixed Gaussian-Lorentzian (Voigt) lineshapes. The transmission function of
 57 the analyser has been carefully determined using clean Au, Ag and Cu foils, whilst the work function of the analyser
 58 was determined using the Fermi edge of a polycrystalline Ag sample at regular intervals throughout the experiment,
 59 thereby allowing accurate composition and binding energy shifts to be determined. UPS experiments were performed
 60 using an incident beam of He I photons ($h\nu = 21.2$ eV), generated using a HIS 13 VUV source (FOCUS GmbH,
 61 Germany). LEED observations were conducted using a SPECTALEED optic (Omicron Nanotechnology, UK).

62 In-situ sample preparation was conducted with a variety of instruments attached to the vacuum system. Ion
 63 bombardment was conducted at room temperature using an incident beam of 1.5 keV Ar^+ ions, generated using a
 64 FIG 05 ion gun (Omicron Nanotechnology, UK). Atomic hydrogen exposure was facilitated by a TC-50 thermal gas
 65 cracker (Oxford Applied Research, UK) in the attached preparation chamber, with an estimated H_2 cracking efficiency
 66 of 50%. All atomic hydrogen doses were conducted over a 15 minute duration using a pressure of 1×10^{-6} mbar (675
 67 L total per dose [H and H_2 combined]), with the sample held at the chosen temperature for the duration of H dosing

and for a subsequent five minutes in the absence of a H flow. Annealing was achieved using sample heaters located on the manipulators in both the preparation and analysis chambers, with the sample temperature measured using a pre-calibrated chromel-alumel thermocouple.

3. Results & Discussion

3.1. Characterisation of the as-loaded surface

The XPS spectra from the as-loaded samples (typical survey shown in supplementary material, core levels from each sample shown in Figure 1), exhibited the typical atmospheric contamination species observed on the vast majority of samples, including hydrocarbons (285.6 eV), C-OH (287.1 eV), C=O (288.8 eV) and carbonyl groups (289.9 eV) in the C 1s region. These components are all shifted to higher binding energies than the graphitic C 1s peak to which many studies are energy-referenced, but are in line with previous observations of adventitious C on GeO₂ [50, 51]. Hence the internal energy referencing of the spectrometer was used. The Ge 2p_{3/2} region consists almost entirely of a peak due to GeO₂ (1221.6 eV), accompanied by a small component at 1218.1 eV from the underlying bulk Ge. By contrast, the less surface specific Ge 3d region revealed not only a GeO₂ contribution (33.5 eV), but also additional peaks due to germanium sub-oxides (at 31.7 eV and 30.5 eV) [49], and bulk Ge (30.0 eV). This contrast indicates that the thickness of the GeO₂ layer is of the order of the probing depth of the Ge 2p region (i.e. around 26 Å, three times the inelastic mean free path of 8.69 Å for Ge 2p photoelectrons in Ge, compared to 28.88 Å for Ge 3d photoelectrons [52]). The O 1s region also exhibits contributions from Ge oxides and atmospheric contaminants (531.4 eV, 532.9 eV), as well as small contributions from Ge LMM Auger peaks (529.5 eV and 534.8 eV).

3.2. Role of substrate temperature on AHC efficiency

In order to study the effectiveness of atomic hydrogen cleaning for the low temperature removal of surface oxides from the Ge(100) surface, a series of atomic hydrogen doses were conducted at room temperature, 150 °C and 250 °C. The evolution of the core level peaks at the three different treatment temperatures is shown in Figures 2, 3 and 4 respectively. Inspection of panels (a) and (b) in each of these figures reveals the ability of atomic H to react with the surface oxide, leading to an increase in the bulk Ge 2p_{3/2} (1217.5 eV) and 3d (29.4 eV) components, and a corresponding reduction in the thickness of the oxide layer. Whilst the reaction is relatively slow at room temperature (Figure 2), where a small oxide peak is observed after 7425 L atomic H exposure, the rate of oxide removal is significantly faster at elevated temperatures where no oxide components are observed after an exposure of 2700 L. The spectra collected after a 675 L exposure show that 250 °C cleaning proceeds faster, with less oxide intensity at around 33 eV in the Ge 3d region when compared to cleaning at 150 °C. These trends are corroborated by the O 1s spectra, which show complete removal of O from the surface after a 2700 L exposure at elevated temperatures, and decreased O 1s intensity after 675 L in the 250 °C case. The total O:Ge ratio during cleaning at the three temperatures is plotted in Figure 5 to illustrate this behaviour further.

During oxide removal, a downward shift of the clean Ge 3d peaks was clearly observed. In the as-loaded sample, the bulk Ge 3d_{5/2} peak was recorded at 30.0 eV, shifting to 29.5 eV and 29.4 eV following cleaning at 150 °C and 250 °C, respectively. This effect was less pronounced for the sample cleaned at room temperature, where a shift to 29.6 eV was observed. These shifts are indicated by the dashed lines in panel (b) of Figures 2, 3 and 4 and are ascribed to a reduction in the strength of the surface dipole moment which is typically stronger on oxide surfaces contaminated with hydrocarbons and water than on clean surfaces.

Whilst the above demonstrates the ability of atomic H to remove surface oxides from Ge films, it is also important to remove hydrocarbons from the surface which naturally adsorb during exposure to atmosphere. The efficiency with which hydrocarbons are removed is demonstrated via the comparison of panel (d) in Figures 2, 3 and 4. These data clearly show that exposure to atomic H at room temperature removes loosely-bound molecular adsorbates such as CO and carbonyls from the surface, but the more strongly bound hydrocarbons remain, even after exposures in excess of 5000 L. However, at elevated temperatures, hydrocarbons are removed more effectively and are almost completely removed after 3375 L exposure at 250 °C.

In order to establish whether the removal of surface oxides and adsorbed hydrocarbons is simply an effect of substrate temperature, or the combined effect of heat and atomic H, Figure 6 shows a series of 20-minute anneals performed under UHV conditions (i.e. without atomic H). These data clearly show that whilst some of the more

loosely-bound oxygen and carbon-containing compounds are removed at 250 °C, the surface oxides and majority of the hydrocarbons remain on the surface. Hence it is clear that in order to effectively prepare a Ge surface free from C and O contaminants at relatively low temperatures, a combination of both atomic hydrogen and annealing is required.

3.3. Comparison of contamination removal - AHC vs IBA

Whilst proposing AHC as a viable method for low temperature cleaning of the Ge(100) surface, it is important to compare the surface cleanliness and order to a sample prepared by IBA. Three cycles of ion bombardment were performed using an incident beam of 1.5 keV Ar⁺ ions for 15 minutes, each followed by annealing at 600 °C for 30 minutes under UHV conditions. A comparison of the XPS data acquired at the conclusion of this procedure to the spectra recorded following exposure to 3375 L of atomic H are shown in Figure 7 and Table 1. Here we observe small residual C 1s and O 1s peaks following the AHC treatment (0.50 % and 0.34 % of total composition), whereas these features are absent following the IBA process. However, such small levels of contamination within the sampling depth of the experiment demonstrates that AHC and IBA can achieve surfaces essentially free from contamination. However, it has been shown previously that IBA cleaning results in residual damage in the near-surface region, which can dramatically change the structure and electronic properties of the surface and sub-surface region [53–56].

For certain applications it is important to establish a well-ordered surface as well as the removal of contamination and surface oxides. The LEED patterns observed from the AHC and IBA clean surfaces are shown in Figure 8. Whilst both surfaces exhibit a (2 × 1) pattern at 112 eV, the diffraction features from the IBA-prepared sample are much sharper than from the AHC sample, indicating a slightly more well-ordered surface in the former case. Indeed, here we also observe some streaking between the fractional order spots, indicating disorder in the dimer rows which has been shown previously to form the c(4 × 2) reconstruction at temperatures below 220 K [15]. AHC is a chemical

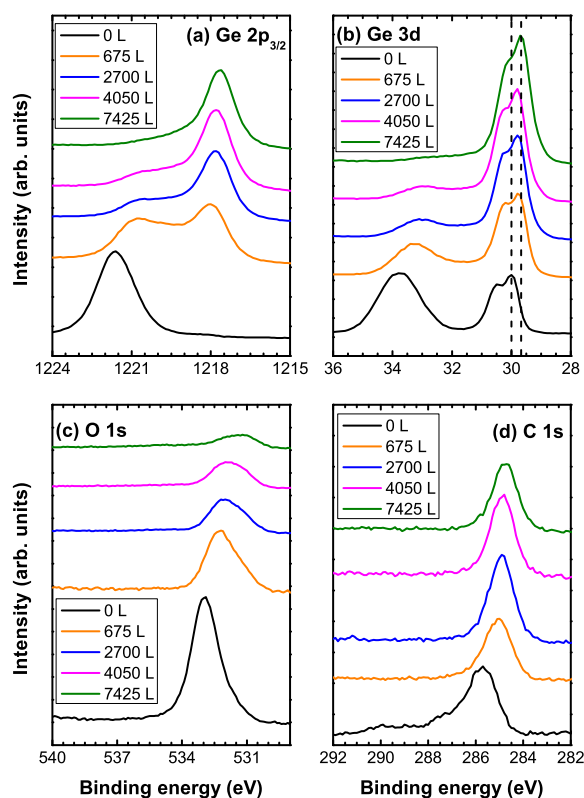


Figure 2. (Colour online) Evolution of the (a) Ge $2p_{3/2}$, (b) Ge $3d$, (c) O $1s$ and (d) C $1s$ regions during exposure to atomic H at room temperature. Both Ge regions show evidence of a downward shift in binding energy of the bulk Ge components. Both Ge regions and the O $1s$ region demonstrate the removal of surface oxides during cleaning, but the C $1s$ region shows that room temperature cleaning is ineffective for hydrocarbon removal.

136 cleaning process which does not provide as much energy to the system in order for atoms to form a well-ordered
 137 surface, and thus a more diffuse LEED pattern could be expected. However, it is also possible that the surface is at
 138 least partially H-terminated, a possibility explored further below.

139 3.4. LEED and UPS measurements from clean and hydrogen-terminated Ge(100) surfaces

140 The optimization of the charge injection process in many modern devices can be achieved through the modification
 141 of the work function of a material [57]. Landemark and co-workers employed a downward shift of 0.2 eV in the work
 142 function of the Ge(100) surface upon hydrogenation when analysing angle-resolved photoemission data [40]. In order
 143 to study this proposed shift in more detail, a Ge(100) film was clean via cycles of 1.5 keV Ar⁺ ion bombardment
 144 and subsequent annealing at 600 °C until a sharp (1 × 1) LEED pattern (Figure 9(a)) was observed, in conjunction
 145 with a work function of 4.67 eV (Figure 10), in agreement with the value given by Landemark [40]. Following IBA
 146 cleaning, the sample was exposed to a 675 L dose of atomic H with the sample temperature held at 250 °C. The post-
 147 hydrogen LEED pattern is shown in Figure 9(b) and exhibits a slight degradation of the surface ordering, with the

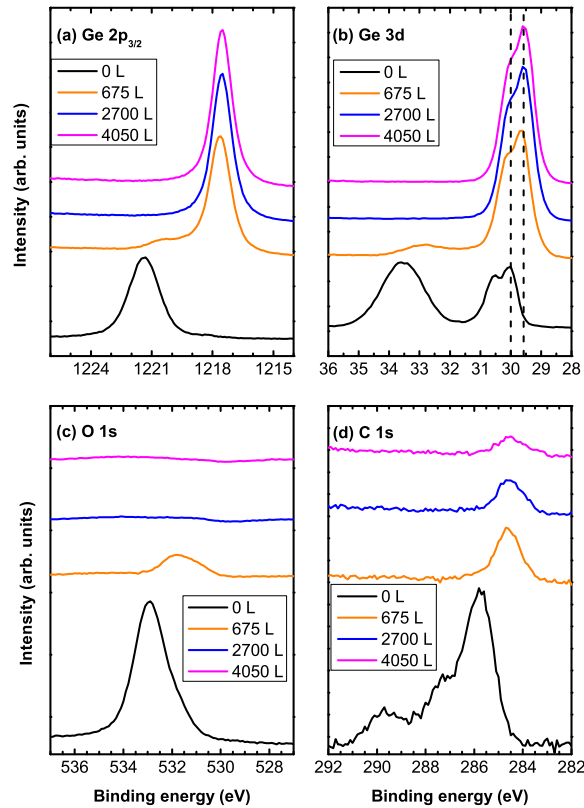


Figure 3. (Colour online) Evolution of the (a) Ge $2p_{3/2}$, (b) Ge $3d$, (c) O $1s$ and (d) C $1s$ regions during exposure to atomic H at 150 °C. Both Ge regions show evidence of band bending at the surface, with a downward shift in binding energy of the bulk Ge components. All regions exhibit more effective contamination removal than the room temperature H exposure.

Table 1. Summary of the compositions of the as-loaded, atomic hydrogen-cleaned and IBA-cleaned samples.

Sample	Ge $3d$ (%)	C $1s$ (%)	O $1s$ (%)
As-loaded	42.50	13.06	44.44
250 °C AHC	99.16	0.50	0.34
IBA	100.00	0.00	0.00

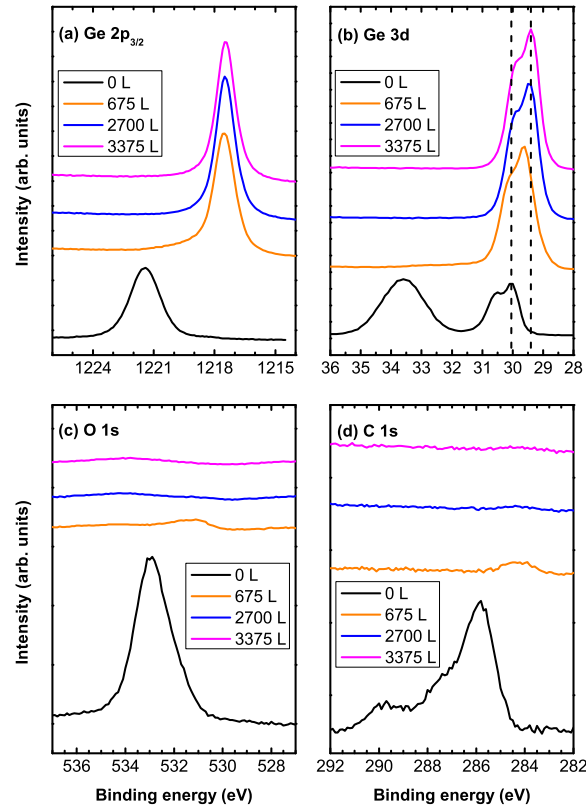


Figure 4. (Colour online) Evolution of the (a) Ge $2p_{3/2}$, (b) Ge $3d$, (c) O $1s$ and (d) C $1s$ regions during exposure to atomic H at 250 °C. Both Ge regions show evidence of band bending at the surface, with a downward shift in binding energy of the bulk Ge components. All regions exhibit more effective contamination removal than cleaning either at room temperature or 150 °C.

148 pattern now more similar to the one produced by AHC (Figure 8(a)). Examination of the UPS data recorded following
 149 H exposure shows a decrease in the work function to 4.34 eV, some 0.33 eV lower than the clean Ge(100)-(2 × 1)
 150 surface, similar to previous observations on Si(100) by Koke and Mönch [58]. Unfortunately it was not possible to
 151 use UPS to accurately determine the work function of the Ge(100) surface prepared by AHC. It is unclear whether
 152 the measured value of 4.50 eV is due to a H termination layer or a small amount of hydrocarbons remaining on the
 153 surface, and the extreme sensitivity of UPS to such contamination.

154 4. Conclusions

155 In this paper we have demonstrated the ability to prepare a clean, well-ordered Ge(100) surface with thermally-
 156 generated atomic hydrogen. This process is far less destructive than surface preparation using ion bombardment and
 157 high temperature annealing, and is thought to preserve the electronic properties of the Ge film. Using XPS it was
 158 found that some of the surface oxide layers were removed by atomic hydrogen at room temperature, but a majority of
 159 the hydrocarbons remain on the surface. As the surface temperature during atomic hydrogen exposure is increased,
 160 the efficiency of the cleaning process improves dramatically. Exposure to 3375 L of atomic H while the surface
 161 is heated to 250 °C led to an almost complete removal of all oxygen and carbon-containing compounds from the
 162 surface, a comparable level of cleanliness to a sample cleaned using IBA. LEED revealed that both the AHC and IBA
 163 prepared surfaces exhibited a (2 × 1) periodicity, implying an asymmetric dimer reconstruction. The IBA sample
 164 yielded sharper diffraction features and streaks between fractional order spots, hinting at the $c(4 \times 2)$ reconstruction
 165 which has been previously observed below room temperature. The work function of the IBA-prepared Ge(100)-(2 ×
 166 1) was found to be 4.67 eV via UPS measurements. This decreased by 0.33 eV upon hydrogen termination, with an

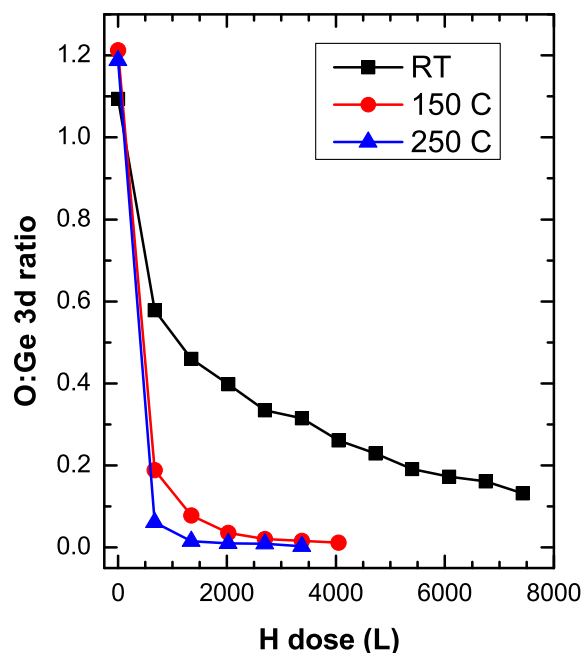


Figure 5. (Colour online) The change in the ratio of the intensity in the Ge 3d and O 1s regions as a function of H exposure at room temperature, 150 °C and 250 °C. The removal of surface contamination and Ge-oxides is much more efficient when the sample is above room temperature, with 250 °C annealing proving to be the slightly more effective condition.

167 associated degradation of the LEED pattern which suggests a degree of disorder in the arrangement of H atoms on the
 168 surface. The results presented here open avenues to enhanced employment of Ge in applications where the removal of
 169 surface oxides, deposition on clean Ge surfaces or the ability to passivate the surface via H-termination are important.

170
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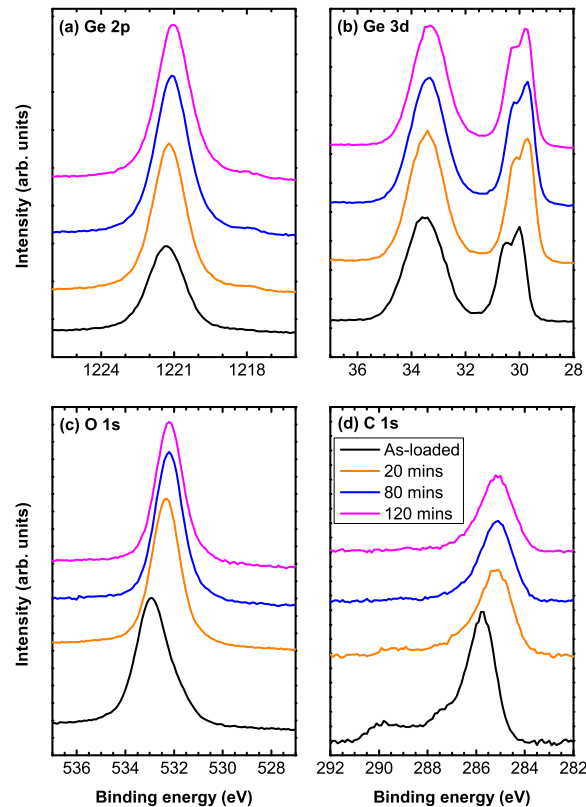


Figure 6. (Colour online) Evolution of the (a) Ge $2p_{3/2}$, (b) Ge $3d$, (c) O $1s$ and (d) C $1s$ regions during annealing at 250 °C under UHV conditions. Note that one annealing cycle of 20 minutes is equivalent in time to an atomic H exposure of 675 L.

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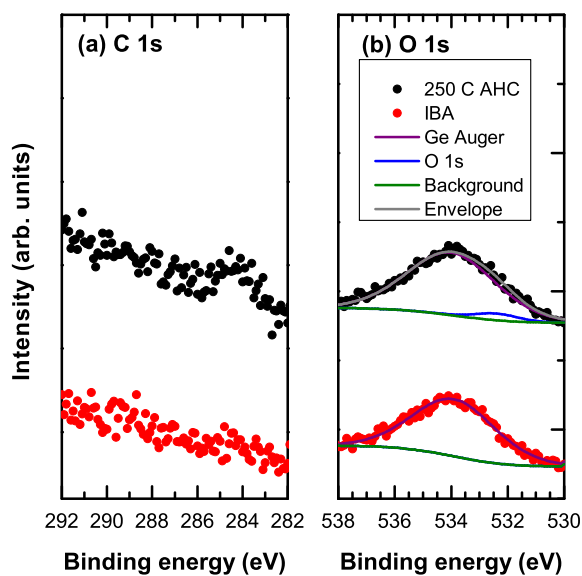


Figure 7. (Colour online) Comparison of (a) the C 1s and (b) the O 1s regions following exposure to 3375 L of atomic H at 250 °C (black dots) and following cycles of room temperature ion bombardment and annealing at 600 °C (red dots). The AHC sample was found to exhibit a small C 1s peak and a very small O 1s shoulder on the Ge Auger peak, unlike the IBA-cleaned sample. Compositional analysis is given in Table 1.

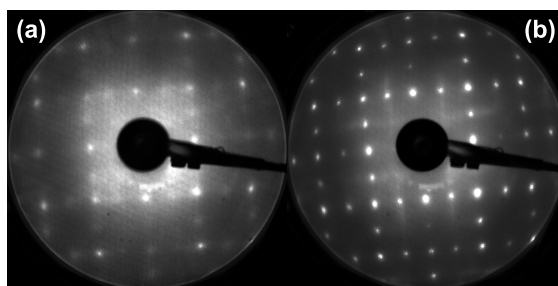


Figure 8. Comparison of the LEED patterns observed at 112 eV following cleaning of the Ge(100) surface using (a) atomic hydrogen cleaning at 250 °C, and (b) cycles of room temperature ion bombardment and annealing at 600 °C. The sharper spots in the IBA-cleaned image suggests a more well-ordered surface.

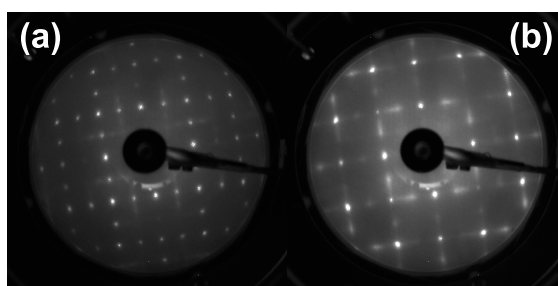


Figure 9. Comparison of the LEED patterns observed at 112 eV (a) following cleaning of the Ge(100) surface using cycles of room temperature ion bombardment and annealing at 600 °C, and (b) following subsequent H-termination at 250 °C. The streaking in the post-hydrogenation LEED pattern suggests some slight degradation in the surface ordering.

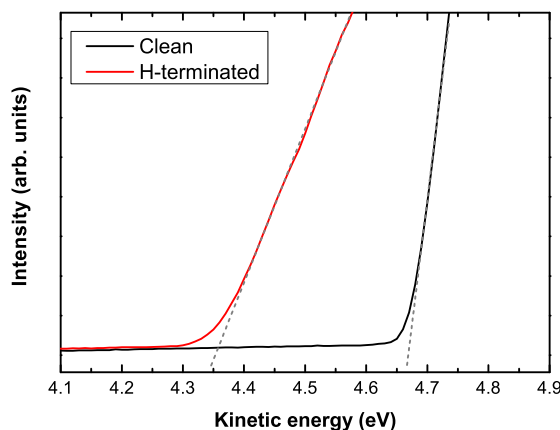


Figure 10. (Colour online) Comparison of the UPS data from the IBA-prepared Ge(100)-(2 × 1) surface (black), and following subsequent exposure to 675 L of atomic H at 250 °C (red). The gray dashed lines indicate extrapolation of the data in order to determine a downward work function shift of 0.33 eV upon hydrogenation of the surface.

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Supplementary Material

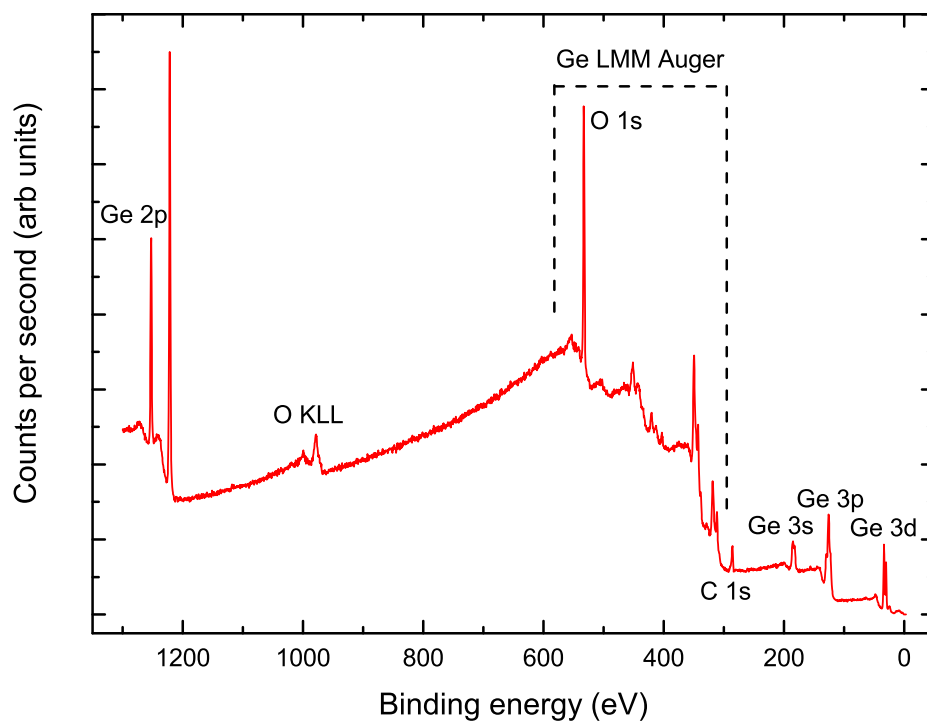


Figure S1: (Colour online) Survey XPS spectrum from the Ge(100) surface prior to atomic hydrogen cleaning, showing the Ge, C and O peaks.