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Gas Phase Formation of Dense Alkanethiol Layers on GaAs(110)

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Abstract: We present a study of the growth and thermal stability of hexanethiol (C6) films on GaAs(110) by direct recoil spectroscopy with time-of-flight analysis. We compare our results with the better known case of C6 adsorption on Au(111). In contrast to the two-step adsorption kinetics observed for Au surfaces after lengthy exposures, data for C6 adsorption on the GaAs(110) surface are consistent with the formation of a single dense phase of C6 molecules at lower exposures. On the contrary, in solution preparation, dense phases can only be obtained on GaAs for long alkanethiols and after lengthy immersions. The C6 layer has a first desorption peak at 325 K, where partial desorption of the alkanethiol molecules takes place. Fits to the desorption curves result in a 1 eV adsorption energy, in agreement with a chemisorption process. Increasing the temperature to 500 K results in the S−C bond scission with only S remaining on the GaAs(110) surface. The possibility of forming dense, short-alkanethiol layers on semiconductor surfaces from the vapor phase could have a strong impact for a wide range of self-assembled monolayer applications, with only minimal care not to surpass room temperature once the layer has been formed in order to avoid molecular desorption.

1. Introduction

Self-assembled monolayers (SAMs) of alkanethiols on semiconductor surfaces are promising two-dimensional systems[1] with interesting technological applications. It is known that these SAMs can passivate III−V semiconductor surfaces,[2] reduce surface states in the band gap,[3] be used as basic elements in molecular electronic devices, and provide reliable immobilization of biomoieties. Alkanethiols can also be used for patterning semiconductor surfaces by dip pen lithography,[4] microcontact printing, and ultrathin electron beam resists.[5] In most of these cases a high and stable coverage by thiols is needed. Hence, research on their adsorption and desorption is relevant. In this research subject, alkanethiols on GaAs can be considered a model system for studying molecular self-assembly on compound semiconductor surfaces. In the literature on the adsorption nature of alkanethiols, high-quality SAMs have been proposed for thiols with a number of C atoms (Cn) equal to or higher than C12.[1,6] They are typically formed by transporting the molecules to the surface either through a solvent or directly via evaporation in a vacuum. In practical semiconductor device fabrication, SAM preparation from the vapor phase is highly desirable as such a process can be integrated with other dry processes such as molecular beam epitaxy and metal−organic chemical vapor deposition to passivate semiconductor surfaces immediately after their epitaxial growth. In these cases, relatively short alkanethiols are preferable because they exhibit a high vapor pressure, and the passivating layer may be removed at a relatively low temperature. Indeed, this insight is shared by three research groups which have worked on vapor phase SAM preparation on GaAs with alkanethiols shorter than C4.[7−9] Their results show that these short alkanethiols are not stable around room temperature and that the formation of a densely packed standing-up phase, which normally provides a better surface passivation, is difficult. To our knowledge, no other research results on the dynamics of vapor phase alkanethiol adsorption on GaAs and subsequent desorption can be found in the literature. Yet the understanding of the adsorption/desorption dynamics is a crucial issue to control SAM quality at a molecular level.

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In this work we focus on the gas phase adsorption of a C6 SAM on GaAs(110) and the adsorption/desorption dynamics in this system. We try to answer the following questions: Is it possible to detect different phases along thiol adsorption? Can we form a dense layer, similar to the standing-up phase formed on Au, using this relatively short alkanethiol? Are the SAMs stable at room temperature? What temperature is needed to remove the molecules from the surface? What elements remain after desorption and annealing? In addition, we also characterize the growth on GaAs as a function of C6 dosage and compare the adsorption/desorption results with those of the better known case of C6 SAM growth on Au(111).

We adopt direct recoiling spectroscopy with time-of-flight analysis (TOF-DRS) as the experimental surface science tool to track the adsorption/desorption nature because of the well-known applicability of this tool for studying atomic/molecular adsorption even at sub-monolayer coverages. A full description of the TOF-DRS technique and its applications has already been reviewed by Rabalais.[10] Briefly, TOF-DRS has the required surface sensitivity[11−13] for the characterization of the adsorption and desorption of organic adsorbates, and it produces little or negligible damage to the organic film. More importantly, TOF-DRS can detect H quantitatively, in addition to C, S, O, and other chemical elements present at the topmost layer. The knowledge of the presence and removal of hydrogen on the surface and near-surface region of a semiconductor is important to device fabrication because it is well-known that H can both beneficially passivate undesirable surface states and detrimentally deactivate useful dopants. In addition, TOF-DRS is also unique, by its nature of differentiating scattering events, in providing some qualitative but yet useful information on the spatial locations of the H and C recoils relative to the surface and other atoms on the C6 molecules. More specifically for the present C6 adsorption case, if the C6 is lying down at the surface, the height variations of all H and C atoms are relatively small, and the probability of the H and C recoils undergoing further scattering (i.e., multiple scattering) prior to their emission from the surface is also relatively small. As such, the TOF signals of these recoils are well defined and the TOF-DRS peaks are expected to be narrow. In comparison, if the C6 is standing up, the H and C atoms near the head of the molecule are relatively far from the outer surface, and as such the recoils of them may undergo multiple scattering and lose some of their kinetic energies prior to their emission from the surface. The TOF-DRS peak of each element will then become a broad envelope spreading toward longer flight times due to the energy loss in the multiple scattering events, an envelope which comprises H or C recoils having different multiple scattering trajectories. This methodology of inferring adsorption features with the systematic direct recoiling peak shape analysis has been employed in a recent study of alkanethiols on Ag(111)[14] and is adopted in the present work. In fact, the experimental results in this work will also exemplify the capability of this technique in differentiating the C6 adsorption nature on Au(111) and GaAs(110).

2. Experimental Section

Gas phase adsorption and growth of a C6 SAM on GaAs(110) were followed by direct recoiling spectroscopy with time-of-flight analysis over an exposure range spanning 6 orders of magnitude. For comparison purposes, measurements under similar experimental conditions were also conducted on sputtered and annealed Au(111).

In order to diminish the strong effect that surface roughness or contamination may have on the adsorption kinetics,[14] we have taken particular care to polish and clean in situ the initial crystalline surface by grazing Ar sputtering (20 keV, 2−3° incidence with respect to surface plane) and annealing to 700 K. During sputtering the sample was kept under continuous rotation around its normal in order to change the azimuthal incidence angle. We have shown before for GaAs(110) that this preparation method results in a well-ordered and flat surface with its overall surface properties being better than those from the method of employing low energy−high angle Ar sputtering and annealing.[15] For the measurements on Au(111), the same preparation method was used. The surface preparation and all measurements were carried out under UHV conditions (10^{-10} Torr with the beam line open). The absence of any surface contamination was verified before and after performing the experiments by TOF-DRS. No O was detected within the limits of the technique at any state of the process of adsorption or desorption.

In the present TOF-DRS measurements, a pulsed 4−6 keV Ar^+ ion beam was directed toward the surface at a fixed incident angle, which was selected within the range of 5° to 35° (with respect to the surface plane). Scattered and surface-recoiled ions plus neutrals were collected by a channeltron electron multiplier mounted with its cone grounded, at the end of a 1.1 m drift tube positioned at a 45° scattering angle.

The hexanethiol was contained in a glass reservoir connected to the chamber through a leak valve. A 6 mm stainless steel tube running from the leak valve to an exit at 3 cm from the sample was used as the doser. This means that the reported exposure values, although expressed in langmuirs with pressure readings corrected by the ion gauge sensitivity, are not calibrated due to the enhanced molecule flux in front of the sample, and they could be different in other systems with different dosage/adsorption geometries. Typical TOF spectra for surfaces covered with a layer of C6 required a total fluence of 10^{10} to 10^{11} ions/cm^2; this low fluence assures the lack of significant damage to the C6 layer.

3. Results and Discussion

In this section we present and discuss the results of applying TOF-DRS to characterize first the initial GaAs(110) substrate, then the adsorption of C6 from the vapor phase on this surface, and finally the thermal desorption of the C6 layer. An important result of this research is that by using the UHV approach to form the C6 layer, the reaction rate is much faster than on Au, while in the solution approach it is much slower. Since this effect may arise from passivation by the surface contamination layer in the solution approach, a careful characterization of the initial substrate prior to the adsorption study is crucial. This is shown in Section 3.1, where the sensitivity of the technique to both cleanliness and top layer relaxation is demonstrated. Then, in Section 3.2, we use the intensity of scattered and recoiled particles as well as the spectral shapes to study the kinetics of adsorption on the GaAs surface and compare it to that on Au-

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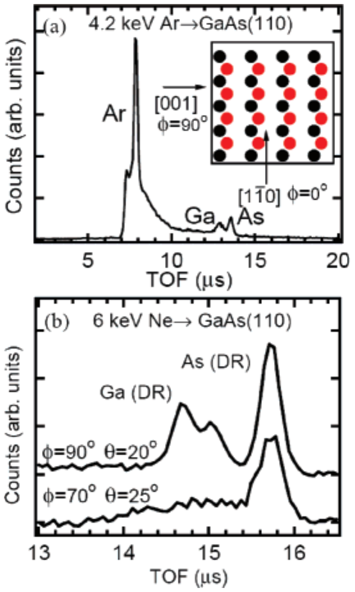

Figure 1. (a) TOF-DRS spectrum for a clean GaAs(110) surface measured along the [001] direction at 20° incidence (θ). The inset shows the schematics of the top view of GaAs(110) and the angle definitions. (b) Detail of the recoiling part of the TOF-DRS spectra for two different incident θ and azimuthal (ϕ) directions. The scattering angle is always maintained at 45°. The absence of the Ga DR peak in the lower spectrum is consistent with the strong surface relaxation.

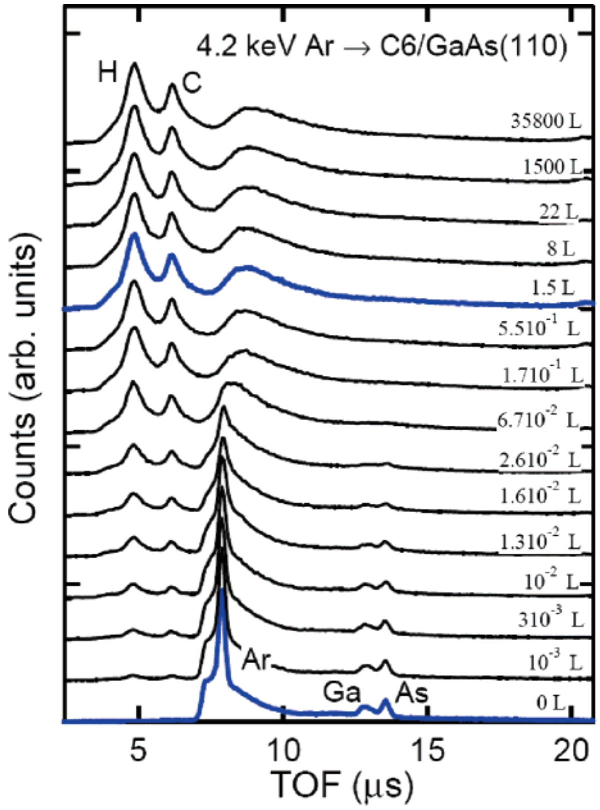

Figure 2. Evolution of the GaAs (110) TOF-DRS spectrum with exposure to the vapors of hexanethiol. The lower thick spectrum (blue) corresponds to the clean surface and the other thick spectrum to the onset of saturation. The dosages are relative, as explained in the Experimental Section.

(111). From the plots of intensity versus dosage we conclude that the C6 dense layer formation takes place without going through a well-defined intermediate layer as is the case for Au. We further conclude from the analysis of peak widths and the general spectral shape that the final C6 layer on GaAs must be formed by molecules in a standing-up configuration, similar to the dense layer formed on Au and that formed from solution in GaAs with longer thiol molecules.[1] Finally in Section 3.3 we present the evolution of the C6 TOF-DRS spectra versus sample temperature. We find a first desorption peak at temperatures slightly higher than room temperature (325 K). The analysis of the spectra shows that at higher temperatures the dense C6 layer is no longer stable, the surface becomes depleted of C and H, and some S is incorporated to the substrate.

3.1. Clean Surface. A typical TOF spectrum for the clean surface taken along $(\theta, \varphi) = (20°, 90°)$, prior to any C6 dosing, is shown in Figure 1a. Here θ is the incident angle measured from the surface plane and φ the azimuthal angle from the [1$\bar{1}$0] direction. The scattering geometry in reference to the top view of the surface is included in the inset. The most prominent peak is the Ar scattering on both As and Ga top surface atoms. The spectral structure corresponding to quasi single scattering superimposes on a broader structure due to multiple scattering. The lack of structures at the left side of the Ar scattering peak (lower TOF) indicates a surface that is clean to better than 1% of monolayer. At the right side of the scattering peak, two peaks are observed and interpreted as Ga and As atoms recoiled into a 45° scattering angle. Here the Ga peak appears broader than the As peak due to the existence of two Ga isotopes with similar abundance. In fact, by changing the scattering experiment design, we can collect scattering spectra with the Ga isotopes clearly resolved, as shown in Figure 1b.

The GaAs(110) surface is an open surface presenting a strong relaxation in which the top As atoms move up by ~0.2 Å and the Ga ones move ~0.5 Å down from the ideal bulk termination. As a consequence of this relaxation, the scattering of ions at low incidence angles is dominated by the top As atoms, while the Ga recoil peak is seen only along a few azimuths, because in most cases outgoing Ga atoms become blocked by their As neighbors (Figure 1b). The surface relaxation is accompanied by charge transfer from the top Ga atoms to the top As atoms, thus offering adsorption sites with different reactivity.

In this work we are interested in following the evolution of the recoiling signals from both adsorbed molecule and substrate atoms versus C6 dosage and versus surface temperature. From the results of Figure 1 we selected the [001] direction for scattering because the As and Ga rows are well separated and equally exposed to the beam. Small molecules adsorbed near one of these rows might change the scattering features from this row but not from the adjacent ones, thus providing information on the surface adsorption structure.

3.2. Adsorption. Figure 2 shows examples of TOF-DRS spectra measured immediately after exposing the clean surface to successive doses of C6 vapors. As the exposure increases from 0 L to more than 10000 L we observe the following:

(a) The Ga and As DR peaks become no longer detectable near 0.1 L.

(b) The Ar scattering from Ga and As decreases and shifts to longer TOF due to multiple scattering effects in the organic layer and in the substrate.

(c) H and C DR are evidenced to the left of the Ar peak.

Beyond 1−10 L, no further changes are seen in the spectra, suggesting that saturation has been achieved. It is interesting to note that, contrary to the case of alkali adsorption on this

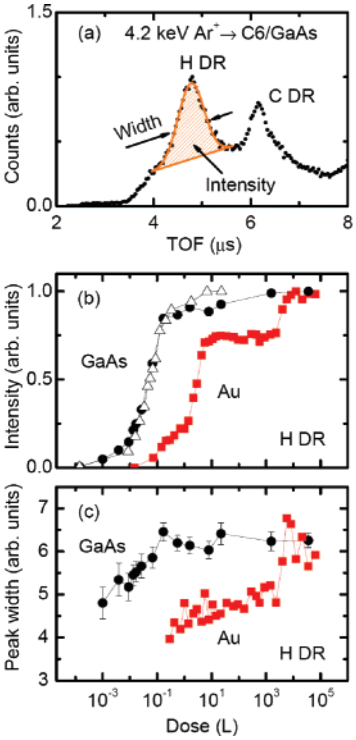

Figure 3. (a) Typical TOF-DRS spectrum acquired under 4.2 keV Ar^+ bombardment of GaAs at high C6 coverage and Gaussian fit to the H direct recoil peak. (b) H recoiling intensity from GaAs(110) (shaded area in a) and Au(111) versus exposure to hexanethiol in UHV. The saturation intensities are normalized to 1. (c) Evolution of the width of the H DR peak versus exposure for both systems (the bars represent the statistical errors).

surface[16] where the rate of decrease of Ga and As DR is different and dependent on the dosage, here both As and Ga DR decrease steadily with exposure and at the same rate. The same observation holds for other azimuthal directions and other incident angles, showing that the C6 molecules cover both Ga and As surface atoms since the beginning of the adsorption process. This observation is compatible with adsorption on both As and Ga rows and discards an adsorption geometry where the molecules would be adsorbed on just one type of surface row (either Ga or As) with the hydrocarbon chain in a plane parallel to it. However, due to the size of the C6 molecules, we cannot discard an adsorption geometry on only one type of row, with the molecules contained in a plane that is not parallel to the rows. Experiments with shorter molecules are necessary to elucidate this point.

The dependence of the H direct recoil intensity (b) and peak width (c) on exposure to the C6 vapors is shown in Figure 3 for both GaAs(110) and Au(111). The intensities were evaluated from TOF spectra as the integral of the recoil peak area, following a background subtraction (shaded area in Figure 3a). The widths were obtained from Gaussian fits of the corresponding recoil peaks (Figure 3a). Two uptake curves measured under similar experimental conditions on different days are shown for GaAs, one ranging from 10^{-3} L to 10^4 L exposure and the other showing larger detail near 0.1 L. Only the intensity for H recoils is shown, since that for C recoils (not shown) follow a very similar trend. The two sets of data points for GaAs show the good reproducibility of the experiment, even though several days of polishing and cleaning cycles were performed on the same substrate between the two adsorptions.

In order to interpret the behavior of the C6/GaAs spectra versus dosage it is convenient to review first the case of Au(111). The uptake curve on Au(111) measured by TOF-DRS (Figure 3b) and the evolution of the width of the H DR peak (Figure 3c) are consistent with the behavior for gas phase deposition on Au determined by different techniques.[17−21] On the basis of this reported behavior, we assign the initial stage for Au (up to 1 L) to thiol adsorption at defects. From 1 L to 10 L the growth of the striped phase of lying-down molecules takes place. This phase may coexist with other intermediate phases in the range 10−1000 L. For exposures of >1000 L, domains of the standing-up phases nucleate and grow rapidly. Finally, for exposures of $>10^4$ L, the dense phases reach saturation. Consistent with this behavior, the width of the recoil peaks changes slowly up to the point where the final dense phase starts to be formed. At this point it increases quickly, reaching a saturation value. As mentioned in the Introduction, the recoil peaks are narrower when the molecules are in lying-down orientations, i.e., when the recoil outgoing trajectories are better defined. For molecule orientations more normal to the surface, the multiple scattering produced in trajectories of C and H recoils starting from different chain positions broadens the observed peaks.

In contrast to this behavior, on GaAs the H and C DR intensity and width increase continuously with exposure until saturation, without showing clear intermediate changes or steps as in Au. This behavior and the fact that the width value of the H DR peak attained already at 1 L is the same as that for the dense SAM phase in Au suggests that the standing-up phase formation on clean GaAs takes place at lower exposures than on Au and without going through well-defined intermediate phases that cover the whole surface, i.e., without going through the ordered lying-down phase. The formation of the dense phase at very low exposures is exactly opposite to what is observed for growth from solution, where lengthy immersions are necessary to form the SAM. These conclusions are further supported below from the comparison of the overall spectral shape for the two cases.

Figure 4 shows the TOF-DRS spectra measured for GaAs(110) at saturation and the corresponding ones for Au(111) in the well-defined lying-down phase (10 L of C6, top panel) and the dense phase (10^4 L, bottom panel). It is well-established that the standing-up phase in Au(111) consists of stable domains of the $(\sqrt{3} \times \sqrt{3})$ and c(4 × 2) surface structures (1/3 monolayer surface coverage) tilted 30° from the substrate normal. Solution deposition leads to a more complex scenario with other intermediate phases in near standing-up configuration[22] but with the same stable surface structures as those described for gas phase deposition. Two dense phases, with tilts of 57° and 14°, have been reported for C18 adsorbed from solution on GaAs-

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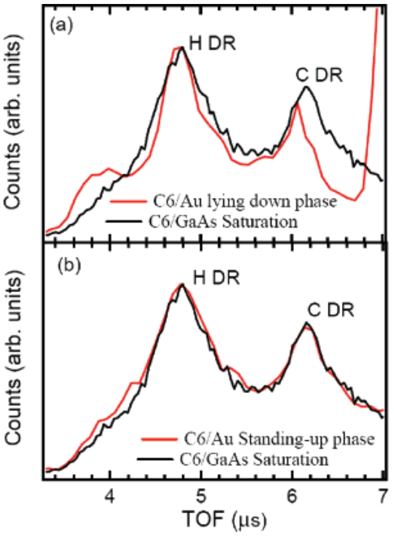

Figure 4. Comparison of the TOF-DRS spectrum induced by 4.2 keV Ar^+ bombardment of C6 on GaAs(110) at saturation with that on Au(111) (a) for the lying-down phase and (b) for the dense phase. Only the H and C recoil peak region is shown. The spectra were normalized at the H peak maximum.

(100),[1] depending on sample-preparation procedures. The close similarity in the whole shape of the spectra for C6 on Au(111) and GaAs at saturation (Figure 4b), i.e.. in the true direct recoil part plus the background below them (due to surface recoiling) and in the position, relative intensity, and width of the individual H and C peaks, suggests that the molecules on GaAs are in a standing-up configuration. Note that for the lying-down phase on Au there is a clear shoulder at the left of the H peak, which corresponds to H surface recoils (i.e., H atoms recoiled first toward the surface). This is smeared out for the more standing-up phase due to multiple scattering and different initial points in the recoil trajectories. At certain low dosages, the GaAs spectra also present this shoulder and similar narrow peaks; however, they keep changing with exposure (in both height and width) while in Au they remain stable for more than 2 orders of magnitude in the exposure. Although the actual tilt of the molecule at present cannot be directly determined from these experiments, the near-standing orientation is qualitatively consistent with the 34° tilt measured for C12 on InP(110),[6] the larger than 15° tilt determined for C12 on GaAs(100),[24] and the 15° tilt measured for C12 and C18, on GaP(110)[6] and GaAs(100),[1] respectively. It can therefore be assumed that the dense SAM phase has been achieved, without passing through stable intermediate phases.

It is interesting to note that, while the growth process reported from solution on GaAs is much slower[1] than on Au, that from the vapor phase reaches saturation at lower exposures than on Au. We believe that the rate difference between the UHV and solution approaches arises because of passivation in the solution approach. Surface passivation such as surface oxide formation or simply solvent molecule adsorption may lead to an increase of the reaction barrier for the formation of C6 chemisorption. The more open GaAs(110) surface and the presence of the dangling bonds may also make the adsorption kinetics from the vapor phase faster than that on Au.

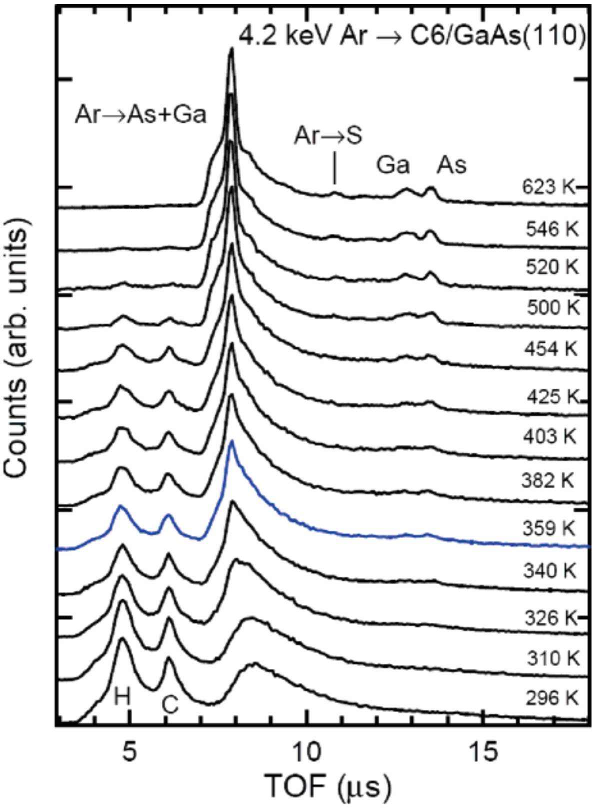

Figure 5. Evolution of the TOF-DRS spectrum with temperature for a C6 covered GaAs (110) surface.

3.3. Desorption. An important part of the information available today for thiol layers grown on semiconductors from the vapor phase comes from thermal desorption experiments. For CH_3SH, $(CH_3S)_2$, and $(CH_3)_2S$ on GaAs(110), Camillone et al.[7] found that CH_3SH desorbs intact near 300 K (311 K for dense CH_3SH layers), and $(CH_3)_2S$ desorbs from the surface at 500 K. For C2 on GaAs(100), two desorption peaks near 370 and 500 K were found.[9] For this case it was proposed that the S−H bond undergoes scission to form ethanethiolate and hydrogen species, both remaining at the surface. The surface products can then either desorb at higher temperatures as thiols or form ethyl species after S−C bond scission. Similar dissociative adsorption and reaction paths were found for C3 on GaAs(100).[8] For C18 on GaAs(100), prepared by immersion, a desorption temperature of $T \approx 390$ K was reported.[1]

In this part of the work we measured TOF spectra for an initially C6-saturated GaAs(110) surface versus sample temperature (Figure 5). The rate of temperature increase was 2 deg/min. The corresponding H DR intensity versus surface temperature is plotted in Figure 6a together with the derivative of the intensity (Figure 6b) and the width of the H DR peak (Figure 6c). For comparison, the H DR intensity measured for Au(111) is also shown. These results are complementary to those from the thermal desorption experiments in the sense that the intensities reported here are proportional to the products remaining at the surface for a given temperature and are thus representative of the coverage. For GaAs (Figure 5) we observe, within the sensitivity of the technique, that both H and C signals

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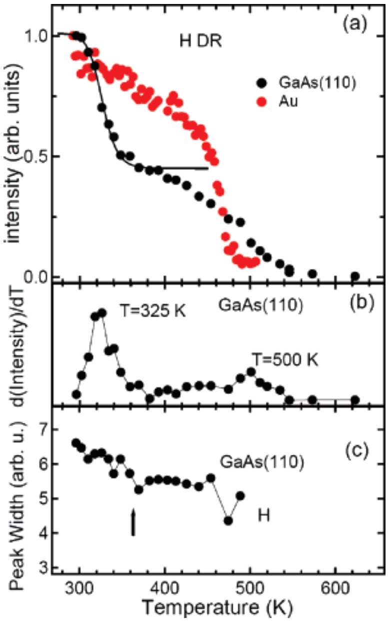

Figure 6. H DR intensities (a), its derivative (b), and peak widths (c) from C6 covered GaAs(110) vs surface temperature. The corresponding intensity for Au(111) is shown for comparison. The solid line in (a) corresponds to a second-order desorption fit.

have the same dependence with *T*. In the initial region, the width of the peaks decreases faster, indicating that the dense C6 layer is changing fast with *T*. Near 350 K, when the H and C DR intensities decrease significantly, the Ga and As intensities become observable, increasing at equal rates. Above 350 K, desorption becomes slower. S starts to be detected at the surface around 400 K, indicating an efficient mechanism for S−C bond scission at higher temperatures. Estimates of the final S coverage vary in the range 5−20% of a ML, depending on whether the adsorption was performed on a sputtered and annealed surface or just after annealing of a C6/GaAs layer (without sputtering in between). This reveals the strong influence on the adsorption kinetics of some preadsorbed S. H and C could be depleted completely above 550 K, while removing S required several cycles of sputtering and annealing.

The drop in the recoil intensity yields a first desorption peak around 325 K, and a second shallower one at 500 K (Figure 6b). The first value is consistent with the lower desorption temperature reported for both shorter alkanethiols prepared from the vapor phase[7−9] and longer alkanethiols prepared from solution.[1] The second value agrees with the value reported by Camillone et al. for the H_3CSCH_3 desorption products..[7] A desorption energy of 1 eV is estimated for the low-temperature desorption peak by using a second-order desorption model and a frequency factor of 10^{13} s^{-1} (continuous line in Figure 6a). This value is consistent with the 0.8 eV value estimated for C1 desorption from the same GaAs face.[7] For the shallow desorption peak at 500 K, a desorption energy of ∼1.5 eV can be estimated, which is similar to that reported by Camillone et al. for H_3CSCH_3.

The two-peaked desorption curve shown for GaAs can be compared with those observed for Au, where the main desorption takes place around 475 K, but short thiol molecules also present a first desorption peak below room temperature.[23] The more open GaAs(110) surface, and the high reactivity of the Ga and As dangling bonds, could allow bonding of both S- and H-head alkanethiol atoms up to above room temperature. It is likely that this peak corresponds to the adsorbed alkanethiol, as has been proposed by Camillone et al.[7] for C1. In contrast, however, the low-temperature phase on Au(111) is physisorbed, and both energy and temperature are strongly dependent on chain length due to van der Waals interactions between chains being comparable with the physisorption energy.[23] Upon raising the temperature, an efficient mechanism for S−C bond scission takes place, leaving at the end only S at the GaAs surface. On Au, the main desorption peak has energies comparable with the 500 K phase on GaAs (1.3 eV from Lavrich et.al.[23] or 1.45 eV from a fitting of the Au desorption curve in Figure 6). The dense SAM layer on Au is more stable than the dense alkanethiol layer on GaAs, not as a result of the desorption energy values but as a result of the significant fraction of molecules desorbed from GaAs near room temperature.

Special attention must be paid to the desorption peak at 325 K. From the gradual decrease in H and C DR intensities between 300 and 325 K, it is clear that even at 300 K a small fraction of molecules desorbs. This is a crucial issue to maintain GaAs surfaces completely protected by the alkanethiol, since exposed surface regions rapidly oxidize. It is therefore possible that the apparently lower SAM packing of C12[24] and shorter alkanethiols,[25] prepared by immersion of GaAs in Cn containing solutions, is the combined result of several factors that could include a small fraction of molecules desorbing at room temperature. The larger intramolecular energy for longer Cn molecules[26] would thus help to explain not only the better SAM quality but also the slightly higher onset temperature for desorption of the low-temperature phase.

Conclusions

We have studied the adsorption and desorption kinetics of hexanethiol (C6) on GaAs(110) from the vapor phase, with time-of-flight direct recoil spectroscopy. Results are compared with C6 adsorption on Au(111) under similar experimental conditions. The main conclusions can be summarized as follows:

(a) The experimental data are consistent with the formation of one alkanethiol phase along the adsorption process. Saturation is obtained after about 1 L of C6. On the contrary, spectra for C6 on Au(111) show a two-phase process, with saturation occurring at much higher exposures (>10^4 L), consistent with results reported in the literature.

(b) H and C direct recoil peaks for both substrates at saturation are comparable in widths and intensities. Therefore, one can conclude that a dense alkanethiol phase of nearly standing-up molecules is formed on the GaAs(110) surface.

(c) The much smaller doses needed for C6 adsorption on GaAs are a direct consequence of the highly reactive nature of the clean (oxide free) GaAs surface. In contrast, in solution, where GaAs oxide removal is difficult, much longer immersion times are necessary than those for Au, and assembly is reported only for longer alkanethiols.

(d) On GaAs, the SAM is stable up to near room temperature. Partial desorption of the thiol molecule takes place near 325 K, while S−C bond scission takes place at higher temperatures

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(>350 K), for the remaining molecules. H and C go away together throughout the whole desorption temperature range.

(e) For the first desorption process, the drop in the H DR intensity versus temperature can be fit with a second-order process, resulting in a desorption energy of ∼1 eV, which indicates that the C6 molecule is chemisorbed. This value is smaller than that reported on Au for the dense thiolate layer, and it explains the lower stability temperature of the dense C6 phase on GaAs.

(f) The formation of dense, short-alkanethiol layers could have a strong impact for a wide range of SAM applications with only minimal care not to surpass room temperature (300 K), once the layer has been formed.

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