Adsorption and Thermal Reaction of Short-chain Iodoalkanes on Ge(100)

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We applied the thermal evolution of XPS spectra to characterize the variation of surface composition during thermal decomposition of CH_3I and to correlate with TPD results to elucidate the reaction intermediates. Figure 1 shows the C 1s and I $3d_{5/2}$ spectra for the Ge(100) surface exposed to CH_3I at 105 K for 150 s and subsequently annealed to various temperatures. All XPS spectra were recorded for samples at 105 K after being heated to a desired temperature at a rate less than 1 K/s and cooled immediately on terminating the heating abruptly. The intensities of C 1s at 285.6 eV and I $3d_{5/2}$ at 621.9 eV due to chemisorbed CH_3I began to attenuate with a similar rate on annealing the sample to 200 K and completely disappeared at 320 K. In contrast, the intensities of features of C 1s at 285.0 eV and I $3d_{5/2}$ at 620.1 eV increase by ~15%. These spectral changes reveal that chemisorbed CH_3I partially desorbs intact from the surface, corresponding to the desorption maximum of CH_3I at 245 K. The remaining CH_3I dissociates to form additional surface CH_3 and I.

Based on the TPD and XPS data, we summarize the adsorption and decomposition of CH_3I according to the following reactions.

1. $CH_3I_{(g)} \rightarrow CH_3I_{(ad)}$ or $CH_{3(ad)} + I_{(ad)}$ 105 K
2. $CH_3I_{(ad)} \rightarrow CH_3I_{(g)}$ or $CH_{3(ad)} + I_{(ad)}$ 200-320 K
3. $CH_{3(ad)} \rightarrow CH_{3(g)}$ 670-770 K
   $CH_{3(ad)} + CH_{x(ad)} \rightarrow CH_{4(g)} + CH_{x-1(ad)}$ (x = 1, 2 or 3)
   $I_{(ad)} + CH_{x(ad)} \rightarrow HI_{(g)} + CH_{x-1(ad)}$
   $I_{(ad)} \rightarrow I_{(g)}$

The adsorption and thermal decomposition of iodoalkanes CH_3I, C_2H_5I and C_4H_9I on Ge(100) were studied with temperature-programmed desorption (TPD) and X-ray photoelectron spectra (XPS) using synchrotron radiation. At 105 K, the iodoalkanes adsorb both molecularly and dissociatively on Ge(100); the shorter-chain iodoalkane dissociates to form a surface alkyl and an I adatom to a greater extent. The chemisorbed iodoalkane gradually dissociates to form a surface alkyl and an I adatom in a temperature range 200-370 K. At 720 K, most surface CH_3 desorbs directly from the surface, and other surface CH_3 radicals undergo disproportionation to desorb as CH_4. Surface C_2H_5 and C_4H_9 mostly undergo -hydride elimination to desorb as C_2H_4 and C_4H_8 at ~550 K, respectively. The temperature for C_4H_9 to react is slightly lower than that for C_2H_5 because the C_4H_9 chain exhibits a stronger interaction with the surface than C_2H_5. The I adatom can react with a H atom liberated during decomposition of a surface alkyl and subsequently desorbs as molecular HI in two temperature regimes, ~650 and ~720 K. Some I adatoms are removed from the surface via direct desorption in atomic form at 720 K. On annealing to 770 K, the Ge surface becomes free of I adatom but retains a deposit of residual C as adatoms. According to our data, the temperature of fabrication and operation of a Ge-based device with the alkyl monolayer is suggested to be not higher than 530 K.

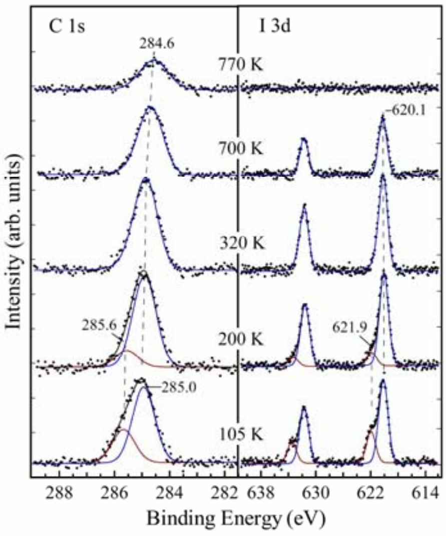

Fig. 1: XPS spectra of C 1s and I 3d for a Ge(100) surface exposed to CH_3I for 150 s at 105 K and subsequently heated to indicated temperatures.

Reference

[1] P. Y. Chuang, W. L., Lee, T. F. Teng, Y. H. Lai, and W. H. Hung, J. Phys. Chem. C **113,** 17447 (2009).