Surface changes on AlH_3 during the hydrogen desorption

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Surface change of $\alpha\text{-AlH}_3$ during the hydrogen desorption was investigated by means of *in situ* x-ray photoelectron spectroscopy combined with thermal desorption spectroscopy. The surface of AlH_3 covered by an oxide layer significantly changes upon hydrogen desorption and the hydrogen desorption rate increases remarkably. In this study, the role of the surface oxide layer on AlH_3 in view of the hydrogen desorption kinetics was investigated. AlH_3 only decomposes into Al and H_2 at the free surface and not in the bulk. Therefore, a closed surface oxide layer prevents the thermodynamically unstable AlH_3 from decomposition. © 2010 American Institute of Physics.

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AlH_3 is a potential solid hydrogen storage material, e.g., for automotive application, because of its high storage capacity with gravimetric and volumetric densities of 10 mass % and $149 \text{ kgH}_2/\text{m}^3$, respectively, and fast desorption kinetics.¹ $\alpha\text{-AlH}_3$ is the most stable among the various polymorphs of AlH_3 .^{2–5,12} The formation enthalpy ΔH ($\text{Al} + 3/2\text{H}_2 \rightarrow \alpha\text{-AlH}_3$) is approximately -10 kJ/mol AlH_3 , which gives the Gibbs formation energy $\Delta G_{298 \text{ K}}$ of $+49 \text{ kJ/mol AlH}_3$.² At ambient temperatures, the formation of AlH_3 from its elements proceeds under a high hydrogen pressure above 25 kbar.^{6,10} However, AlH_3 exhibits a slow desorption kinetics even in vacuum at room temperature. The apparent activation energy for the desorption process ($\alpha\text{-AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$) is reported to be in the range between 102 and 150 kJ/mol.^{7–9} In previous literature, the presence of surface oxide layer has been assumed to inhibit the decomposition of the embedded AlH_3 .¹⁰ Sandrock *et al.*¹¹ reported that an alkali-metal hydride dopant lowers the desorption temperature significantly. They proposed a reaction model in which an alanate phase formed by MAIH_4 on AlH_3 enhances the hydrogen desorption through the surface oxide layer.¹¹ In the further decomposition process, the nucleation and growth of Al phase in two and three dimensions is reported to be the rate controlling step in the decomposition of AlH_3 .⁸ Although the phenomenological model can explain basic observations, the direct evidence was missing. In this study, we performed *in situ* x-ray photoelectron spectroscopy (XPS) surface analysis during decomposition of $\alpha\text{-AlH}_3$ in order to elucidate surface processes of AlH_3 covered by oxide layers with respect to hydrogen desorption mechanism.

AlH_3 particles were prepared by the chemical reaction between LiAlH_4 and AlCl_3 in ether solution.^{3,12} *In situ* XPS surface analysis combined with thermal desorption spectroscopy (TDS) was performed in a modified VG EscaLab spectrometer with a base pressure below 10^{-10} mbar. The sample pellet was prepared inside an Ar glove box ($\text{O}_2 < 1 \text{ ppm}$ and $\text{H}_2\text{O} < 0.1 \text{ ppm}$) directly connected to the spectrometer and transferred without exposure to ambient conditions. The XPS

spectra were collected with a SPECS PHOIBOS 100 analyzer using a nonmonochromated x-ray source (Mg $K\alpha$: 1253.6 eV, Al $K\alpha$: 1486.6 eV). The instrument was calibrated to the Au $4f_{7/2}$ level (84.0 eV binding energy). Intensity was adjusted by relative sensitivity factor, transmission function, kinetic energy, and escape-depth.¹³ The simultaneous TDS measurement was carried out by resistive heating with a temperature ramp of 0.5 K/min.

Figure 1(a) shows the TDS spectrum of the decomposition of AlH_3 under ultrahigh vacuum (UHV) condition and with a temperature ramp of 0.5 K/min. No noticeable changes in the amounts of H_2O and O_2 evolved were observed in the range of the partial pressures $< 10^{-9}$ mbar during the decomposition [not shown in Fig. 1(a)]. Significant

FIG. 1. (a) Changes in hydrogen partial pressure by TDS (0.5 K/min) and (b) intensity ratio of Al 2p to O 1s in *in situ* XPS during decomposition of AlH_3 .

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FIG. 2. Change in XPS core level spectra of Al 2p during the hydrogen desorption with TDS (0.5 K/min). The spectra are shown from 313 K up to 388 K (in steps of 5 K).

hydrogen desorption from the surface of AlH_3 starts around 360 K without any significant amount of H_2O evolution, namely, without reduction of the oxide layers. Figure 1(b) shows the surface change of AlH_3 during the hydrogen desorption process measured by *in situ* XPS where the change in intensity ratio of Al 2p to O 1s is shown. The atomic concentrations (excluding H) in the surface region of AlH_3 were 62.0 at. % (Al), 32.3 at. % (O) and 5.7 at. % (C) at 306 K, and 67.2 at. % (Al), 25.4 at. % (O) and 7.4 at. % (C) at 388 K. With increase in the hydrogen desorption rate [in Fig. 1(a)], the intensity of Al to O in the surface layers increases. The result clearly indicates that the hydrogen desorption rate is determined by the surface oxide layer of AlH_3 , which hinders the hydrogen desorption at a lower temperature below 350 K. Figure 2 shows the change in core level spectra of Al 2p during decomposition of AlH_3 . With increase in the hydrogen desorption rate [in Fig. 1(a)] and increase in the atomic concentration of Al to O at the surface [in Fig. 1(b)], a new peak appears with the chemical shift of -3.0 eV binding energy. The hydroxide $\text{Al}(\text{OH})_3$ is unstable in UHV at ambient temperature, which decomposes to Al_2O_3 .¹⁴ The observation matches the expected chemical shift between the metallic state (Al: 73.0 eV)¹⁵ and the oxide (Al_2O_3 : 75.8 eV).¹⁵ In a recent microscopic study of α - AlH_3 , Ikeda *et al.*,¹⁶ observed a precipitation/grain-growth of metallic-Al of size 1–50 nm inside the particles surrounded by an Al_2O_3 shell during the decomposition process. Muto *et al.*¹⁷ determined the surface layer covering the AlH_3 particle as amorphous Al_2O_3 with a thickness of 3–5 nm by means of electron energy-loss spectroscopy. Maehlen *et al.*⁹ observed significant anisotropic volume expansion of α - AlH_3 prior to the decomposition by using *in situ*-synchrotron x-ray diffrac-

FIG. 3. (Color online) Mechanism of hydrogen desorption from the surface of AlH_3 (schematic). (a) inhibition of hydrogen desorption by surface oxide layers, e.g., Al_2O_3 (b) breaking of surface oxide layers (c) recombination of hydrogen and growth of metallic Al phase.

tion. The observed volumetric thermal expansion of α - AlH_3 ($5 \times 10^{-5}/\text{K}$) is significantly larger than that of amorphous and crystalline Al_2O_3 [$(0.9-2) \times 10^{-5}/\text{K}$].^{9,18–20} The complete coverage of the AlH_3 by the amorphous Al_2O_3 prevents the recombination of hydrogen, i.e., the formation of hydrogen molecules. The recombination of hydrogen atoms to molecules is only possible at a hydride/gas interface. The greater thermal expansion of AlH_3 compared to that of Al_2O_3 leads to the formation of cracks in the oxide layer upon temperature increase and, therefore, to AlH_3 surface exposed to the gas phase. Our *in situ* XPS study suggests that breaking of the oxide layers formed on AlH_3 is responsible for the marked increase in desorption rate of hydrogen molecules from the surface layers and the growth of the metallic Al phase (as shown in Fig. 3). This is consistent with the reaction model proposed by Sandrock *et al.*¹¹ Since the Al–Al distance in Al metal (2.86 Å) is shorter than that in α - AlH_3 (>3.24 Å), the formation of metallic Al layers underlying the surface oxide layers leads to a further increase of the exposed hydride surface during the desorption process.^{5,9} Therefore, the oxide layer which covers the AlH_3 and inhibits the recombination of hydrogen at the hydride surface breaks up, due to the different thermal expansion of the hydride and oxide, resulting in the desorption of the hydrogen molecules.

In conclusion, the surface changes of AlH_3 during hydrogen desorption were investigated by means of *in situ* XPS combined with TDS. The hydrogen desorption only starts when the surface oxide layer breaks and free AlH_3 surface gets in contact with the gas phase. This is because the bonding states of hydrogen in the hydride are fully occupied and therefore an overlap of neighboring hydrogen atoms in bulk AlH_3 only leads to the occupation of antibonding states. Only at a free hydride surface the metal-hydrogen distance can increase and allow an attractive overlap of the electrons with the ones from an other hydrogen atom by occupying bonding states. The compact oxide layer, therefore, prevents the desorption of hydrogen not for kinetic reasons, e.g., diffusion, but because of chemical reason. Therefore, the AlH_3 covered with a dense oxide layer is thermodynamically stable and hydrogen release only starts when the oxide layer breaks up due to thermal volume expansion of the underlying bulk AlH_3 .

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