THE UNIVERSITY OF WARWICK

University of Warwick institutional repository: http://go.warwick.ac.uk/wrap

This paper is made available online in accordance with publisher policies. Please scroll down to view the document itself. Please refer to the repository record for this item and our policy information available from the repository home page for further information.

To see the final version of this paper please visit the publisher's website. Access to the published version may require a subscription.

Author(s): Tomoya Konishi, Takashi Toujyou, Takuma Ishikawa, Gavin R. Bell and Shiro Tsukamoto

Article Title: Organopalladium catalyst on S-terminated GaAs(001)-(2×6) surface

Year of publication: 2009

Link to published version:

http://dx.doi.org/10.1116/1.3193687

Publisher statement: The published version can be found at Konishi, T. et al. (2009). Organopalladium catalyst on S-terminated GaAs(001)-(2×6) surface. Journal of Vaccum Science and Technology B, vol. 27, pp. 2206-2208.

Organopalladium catalyst on S-terminated GaAs(001)-(2×6) surface

Tomoya Konishi¹, Takashi Toujyou¹, Takuma Ishikawa¹,

Gavin R. Bell² and Shiro Tsukamoto^{1,*}

¹Anan National College of Technology, Tokushima 774-0017, Japan. ²Department of Physics, University of Warwick, Coventry, CV4 7AL, UK.

Organopalladium molecules, such as Pd(CH₃COO)₂ ({Pd}), immobilized on the S-terminated GaAs(001), termed GaAs-S-{Pd} have high catalytic activity and cycle durability in the Mizoroki-Heck reaction. It is thought that the presence of Ga-S bonds in the single atomic layer S-termination is essential for these catalytic properties despite the much higher thickness (~100 nm) of the {Pd} films. In this study, we demonstrate the retention of Ga-S bonds in ultra-thin GaAs-S-{Pd} by using reflection high-energy electron diffraction (RHEED) and scanning tunnelling microscopy (STM). The ultra-thin GaAs-S-{Pd} was prepared by using a vapour-deposition technique. Deposited {Pd} was observed as ~1 nm dot-like structures with STM. The adsorption rate of {Pd} was also investigated.

Keywords: Molecular beam epitaxy: A3, Catalyst materials: B2, Organometals : B1 Pacs codes: 61.05.jh, 68.37.Ef, 82.45.Jn, 82.65.+r

Material names: GaAs, Pd(CH₃COO)₂, S

*Corresponding author: 265 Aoki Minobayashi, Anan, Tokushima 774-0017, Japan. Phone/Fax: +81-884 23 7253. E-mail: tsukamot@anan-nct.ac.jp

Introduction

An unusual, highly active and re-usable heterogeneous catalyst for the Mizoroki-Heck reaction [1.2] has been discovered recently [3-5], best described as the three-component system GaAs-S-{Pd}. The Mizoroki-Heck reaction is one of the important organic reactions forming a C-C bond and is widely used for drug discovery sciences and pharmaceutical industries [6]. The substrate for GaAs-S-{Pd} is S-terminated GaAs(001)-(2×6) (GaAs-S), produced by immersion of GaAs(001) wafers in NH_4S_x solution [3,7] or vapour-deposition of S [8,9]. $Pd(CH_3COO)_2$ ({Pd}) is dissolved in acetonitrile and deposited on the GaAs-S substrates by immersion, resulting in structured Pd-containing thin films which repeatedly give nearly 100 % yield in the Mizoroki-Heck reaction [4]. On the other hand, deposited {Pd} on other surfaces has so far shown poor catalytic properties. For example, poor catalytic activity is realised on the S-terminated Si surface and poor cycle durability occurs on the S-terminated Au or non-terminated GaAs(001) [10]. Although emphasis is placed on the S-termination before the immobilization of {Pd} for the GaAs-S-{Pd} to exhibit the fascinating catalytic property [3,5], the surface molecular structure including Ga-S bonds after immobilization of {Pd} has not yet been investigated. It is vital to examine further the surface molecular structure of GaAs-S-{Pd} by employing the tools of analytical surface science to begin to understand the mechanism of the high catalytic activity in this unique system. In this paper we demonstrate the vapour-deposition of {Pd} on a GaAs-S surface and report surface observations with reflection high-energy electron diffraction (RHEED) and scanning tunnelling microscopy (STM) in an ultra high vacuum (UHV).

Experimental procedures

The sample preparation and the measurements were completely performed in a UHV molecular beam epitaxy (MBE) chamber equipped with RHEED and STM as described elsewhere [11]. Pieces (11×13×0.6 mm³) of GaAs(001), which were cut out from a wafer, were used as

substrates. First the surface of the substrate was thermally cleaned to remove the oxide layer under 1×10^{-4} Pa of an arsenic atmosphere in a MBE chamber. Next, GaAs buffer layer was grown on the surface by MBE until atomically smooth surface was obtained. The substrate was cooled to room temperature to form c(4×4) reconstruction.

The substrate was transferred to a load lock chamber to terminate the $c(4\times4)$ surface with S. The surface was exposed to 1×10^{-3} Pa of S vapour for 5 min. The substrate was again transferred to the MBE chamber and was annealed at 400 °C for 12 h in a UHV. The substrate was subjected to RHEED and STM observation to confirm the formation of S-terminated GaAs(001)-(2×6) reconstruction [9,12] and the absence of any contamination on the S layer.

The vapour deposition of $\{Pd\}$ on the GaAs-S surface was then performed in the load lock chamber. For the vapour deposition of $\{Pd\}$ we prepared a sublimation cell by using a tubular ceramic crucible wound by a tungsten wire heater. Since powdered $\{Pd\}$ sublimates as a trimer at 155 °C [13], this cell was designed for the thermal stability in the range of 120 – 180 °C. We confirmed the sublimation of $\{Pd\}$ in this temperature range by Arrhenius behaviour of the vapour pressure. The substrates were then vapour-deposited with $\{Pd\}$ by the cell at the partial pressure of 6×10^{-5} Pa for 4 s and 8 s. These conditions correspond to supplying at least ~1 and ~2 ML of $\{Pd\}$, respectively, on the basis of the atomic pair density of GaAs(001).

The GaAs-S-{Pd} sample was again transferred to the MBE chamber and was heated up to 100 °C for RHEED measurement and STM observation with tip bias voltage -2.8V and set-point current 0.2 nA.

Results and Discussion

Figure 1 and 2 show that the RHEED patterns of the substrate surface before and after the deposition of {Pd}, respectively. From the brightness line profile analysis, the patterns indicated (2×6) reconstruction brought by S-termination. The deposition of {Pd} did not add any other electron diffraction pattern to the (2×6) pattern. This may be due to the low coverage of {Pd} (Table 1) or that

the deposited {Pd} did not form any periodic structure. Moreover, the pattern did not change by the vapour-deposition of {Pd}. Similar results were obtained when the amount deposited was increased much more. This implies that vapour-deposition of {Pd} did not corrupt the (2×6) reconstruction. It is known that the uniform surface with (2×6) reconstruction shows better stability of {Pd} in GaAs-S-{Pd} than roughly S-covered surface [3].

Figure 3 shows the STM images of the substrate surface after the vapour-deposition of {Pd} for 4 s and 8 s. The dimer rows of S were clearly observed in the background. The line profile along the [1-10] direction suggested the dimer row spacing of ~0.8 nm by the (2×6) reconstruction of S-terminated surface. The STM images also show scattered dot-like structures, which were not observed before the deposition, on the background S-dimer rows. The (2×6) reconstruction structure near the dot-like structure was not corrupted. As the line profile pattern across the dot-like structure is also superimposed on Fig. 3(a), the typical size of the dot-like structures was ~1 nm width and ~0.2 nm height. On the surface with 8 s deposition the dot-like structures were observed more with some clusters in places than that with 4 s deposition. The estimation of amount supplied, amount deposited and adsorption rate of {Pd} on the GaAs-S surface is presented in Table 1. The amount deposited increased depending on the amount supplied. The coverage rate was estimated to be ~2 % for the both deposition conditions.

The similar width dimension (~1 nm) of the dot-like structures observed in Fig. 3 is found in the literature [14]. They report the STM investigation of *in situ* complexation of {Pd} by a monolayer of a bipyridine derivative at a graphite surface. In their work, a {Pd} molecule is known to have the dimension of ~1 nm width with STM. Therefore, accounting for their number density and width dimension, the dot-like structures in Fig. 3 are very likely to be {Pd} molecules.

The STM line profile pattern was also investigated on the {Pd} molecule placed on a cleavage surface of a highly oriented pyrolytic graphite (HOPG) piece. Since the similar profile height (~0.2 nm) was also measured on the {Pd} molecule on the HOPG surface to that on the GaAs-S surface known from the line profile in Fig. 3(a), the {Pd} molecules are settled on the S reconstruction

layer without corrupting or substituting it. This is consistent with the RHEED results that (2×6) reconstruction pattern is remaining after the deposition of {Pd}.

From the RHEED and STM investigations, it was concluded that the {Pd} molecules are immobilized on the GaAs-S surface with preserving the (2×6) reconstruction structure and hence the substructural Ga-S bonds. This result supports the assumption that the S-termination and Ga-S bonds are essential for the high catalytic activity and stability of GaAs-S-{Pd} catalyst [3,5].

Generally S is known as a catalyst-poison that significantly deactivates organometallic catalysts because of the formation of a strong metal-S bond [15]. It is interesting that GaAs-S-{Pd} keeps high catalytic activity and stability even with the presence of S. The evidence of preserving S layer after immobilization of {Pd} on GaAs-S-{Pd} surface may also give one of the important clues to understand the mechanism. The (2×6) reconstruction consists of five S-S adatom dimers, one missing dimmer and strong Ga-S bonds [16], satisfying the local-charge neutrality in themselves [9]. Because the electrons of S are attracted by Ga in Ga-S bonds, it is probable that the binding affinity of S and Pd are moderated so that Pd should easily separate from S to participate in chemical reactions. Further discussion needs more information on the electronic structure of Ga-S bonds by vibrational spectroscopic analyses or molecular orbital calculations.

Conclusion

Pd(CH₃COO)₂ was vapour-deposited on S-terminated GaAs(001)-(2×6) surface. The RHEED patterns and STM images showed that Pd(CH₃COO)₂ molecules were immobilized on the surface with preserving the (2×6) reconstruction structure and hence the substructural Ga-S bonds. This supports the assumption that the high catalytic activity and stability is owing to the amount of Ga-S bonds. The result is potentially one of the important clues to understand the mechanism of the high catalytic activity and stability of the GaAs-S-{Pd} catalyst.

Acknowledgments

This research was partially supported by Japan Science and Technology Agency (JST). The author (T. K.) would like to thank Dr. Nagatoshi Nishiwaki for the valuable discussion on catalyst-poison effect of GaAs-S.

References

[1] T. Mizoroki, K. Mori, and A. Ozaki, Bull. Chem. Soc. Jpn. 44 581 (1971).

[2] R. F. Heck and J. P. Nolley, J. Org. Chem. 37(14) 2320 (1972).

[3] I. Takamiya, S. Tsukamoto, M. Shimoda, M. Arisawa, A. Nishida, and Y. Arakawa, Jpn. J.Appl. Phys. 41 L1197 (2002).

[4] M. Arisawa, M. Hamada, I. Takamiya, M. Shimoda, S. Tsukamoto, Y. Arakawa, and A. Nishida, Adv. Synth. Catal. 348 1063 (2006).

[5] N. Nishiwaki, M. Shimoda, T. Konishi, and S. Tsukamoto, Appl. Phys. Exp. 2 051002 (2009).

[6] M. Larhed and A. Hallberg, Drug Discovery Today 6(8) 406 (2001).

[7] M. S. Carpenter, M. R. Melloch, M. S. Lundstrom, S. P. Tobin, Appl. Phys. Lett. 52 2157 (1988).

[8] N. Koguchi, K. Ishige and S. Takahashi, J. Vac. Sci. Technol. B 11 787 (1993).

[9] S. Tsukamoto and N. Koguchi, Appl. Phys. Lett. 65 2199 (1994).

[10] I. Takamiya, S. Tsukamot, M. Shimoda, N. Miyashita, and M. Arisawa, Chem. Lett. 33(9)1208 (2004).

[11] S. Tsukamoto and N. Koguchi, J.Cryst.Growth 201/202 118 (1999); 209 258 (2000).

[12] J. Suda, Y. Kawakami, S. Fujita, and S. Fujita, Jpn. J. Appl. Phys. 35 L1498 (1996).

[13] H. Schäfer, C. Brendel, H. Rebeneck, and E. Schibilla, Z. Anorg. Allg. Chem. 518 168 (1984).

[14] M. M. S. Abdel-Mottaleb, N. Schuurmans, S. D. Feyter, J. V. Esch, B. L. Feringa, and F. C. D. Schryver, Chem. Commun. 1894 (2002).

[15] J. K. Dunleavy, Platinum Metals Rev. 50(2) 110 (2006).

[16] H. Oigawa, J.-F. Fan, Y. Nannichi, K. Ando, K. Saiki, and A. Koma, Jpn. J. Appl. Phys. 28L340 (1989).

List of table and figure captions

- Table 1. Estimation of amount supplied, amount deposited and coverage rate of {Pd} by vapour-deposition.
- Figure 1. RHEED patterns of GaAs-S surface before vapour-deposition of {Pd}.
- Figure 2. RHEED patterns of GaAs-S surface after vapour-deposition of {Pd}.
- Figure 3. STM images of GaAs-S surface after vapour-deposition of {Pd} for (a) 4 s and (b) 8 s. Line profile pattern along the line marker is also superimposed.

Table 1. Estimation of amount supplied, amount deposited and coverage rate of {Pd} by vapour-deposition.

Deposition time	Amount supplied	Amount deposited*	Coverage rate
4 s	$6.0 \times 10^{14} \text{ cm}^{-2}$	$9 \times 10^{12} \mathrm{cm}^{-2}$	~2 %
8 s	$1.2 \times 10^{15} \text{ cm}^{-2}$	$2 \times 10^{13} \mathrm{~cm}^{-2}$	~2 %

* Estimated form the STM images.





 $Figure \ 1. \ RHEED \ patterns \ of \ GaAs-S \ surface \ before \ vapour-deposition \ of \ \{Pd\}.$





 $Figure \ 2. \ RHEED \ patterns \ of \ GaAs-S \ surface \ after \ vapour-deposition \ of \ \{Pd\}.$



Figure 3. STM images of GaAs-S surface after vapour-deposition of {Pd} for (a) 4 s and (b) 8 s. Line profile pattern along the line marker is also superimposed.