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

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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

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Material names: GaAs, Pd(CH₃COO)₂, S

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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 \times 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 \times 13 \times 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 $c(4 \times 4)$ reconstruction.

The substrate was transferred to a load lock chamber to terminate the $c(4 \times 4)$ 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 structure 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 dimer 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

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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. Tsukamoto, 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.* 28 L340 (1989).

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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	$6.0 \times 10^{14} \text{ cm}^{-2}$	$9 \times 10^{12} \text{ cm}^{-2}$	~2 %
8 s	$1.2 \times 10^{15} \text{ cm}^{-2}$	$2 \times 10^{13} \text{ cm}^{-2}$	~2 %

* Estimated from the STM images.

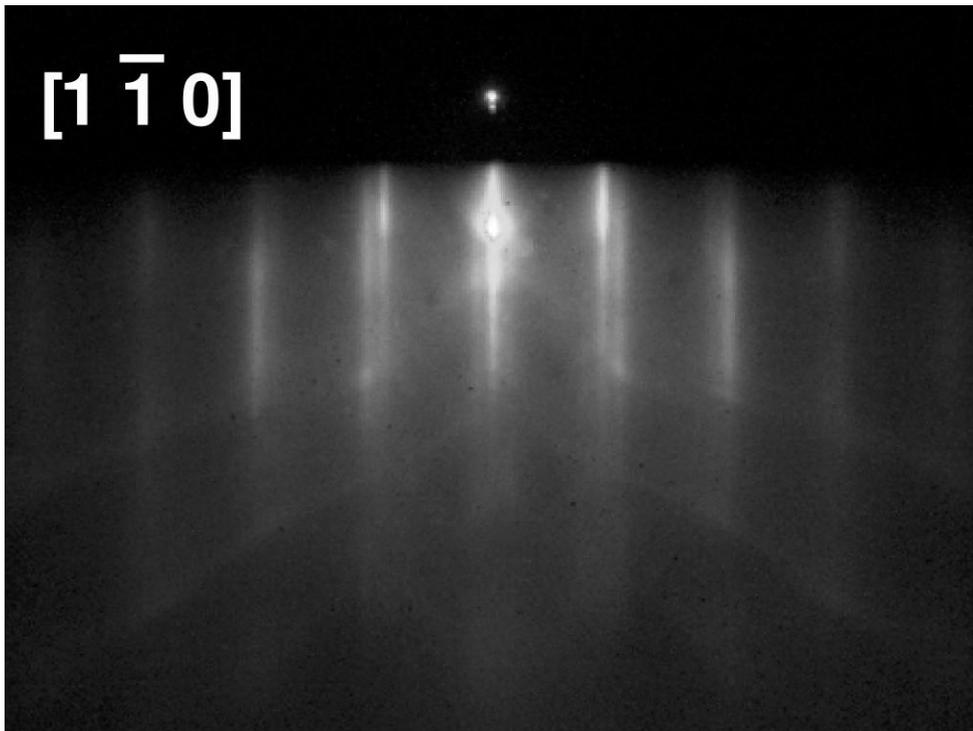
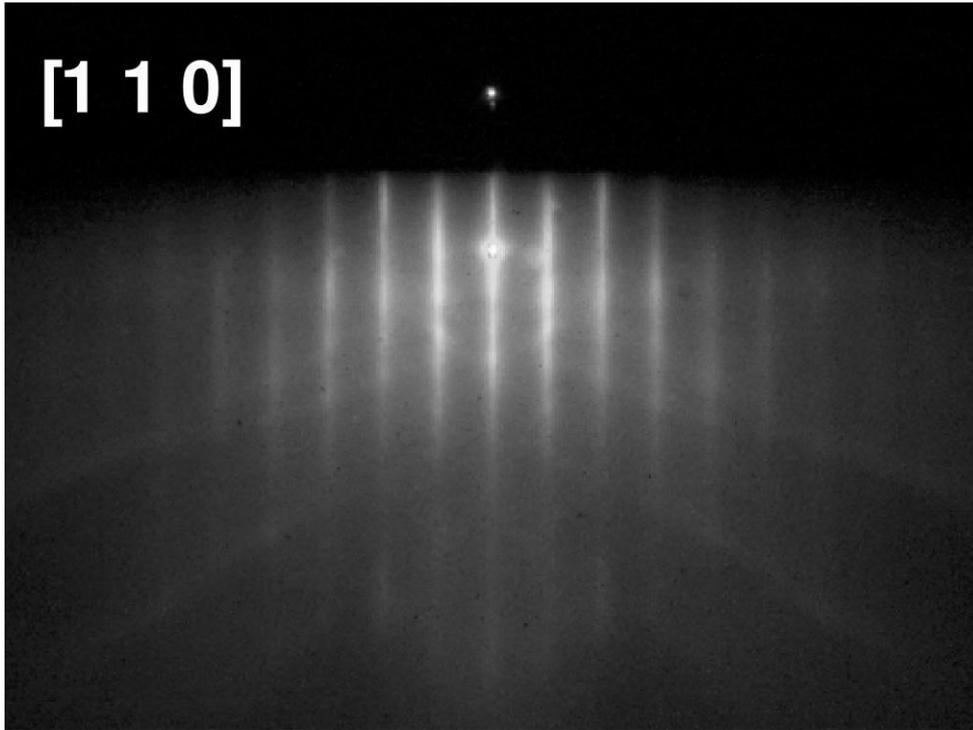


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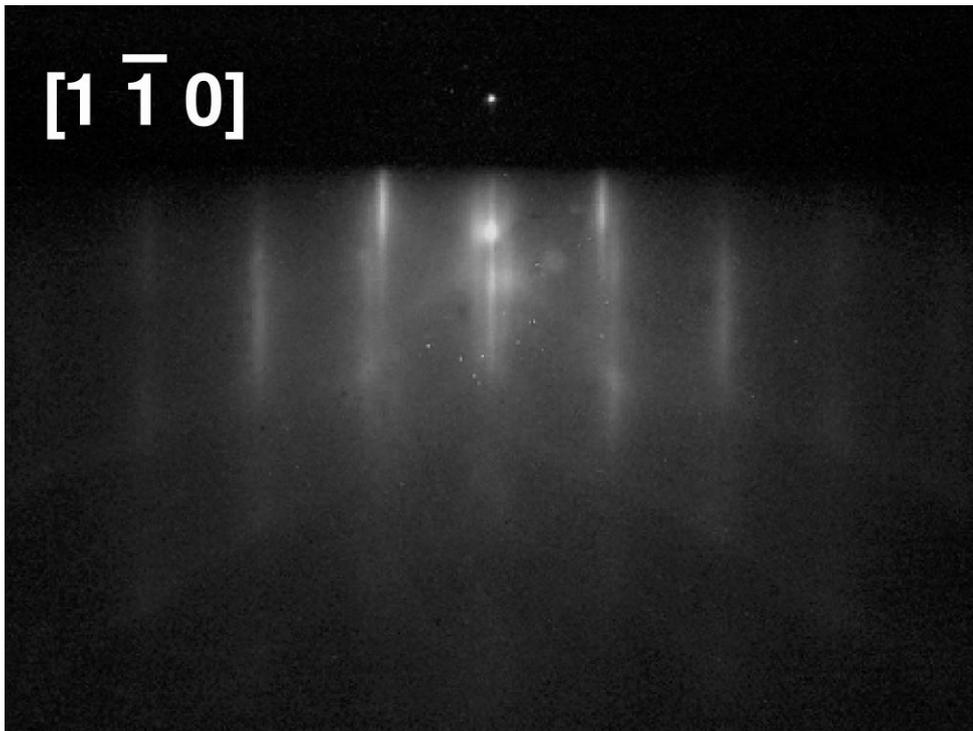
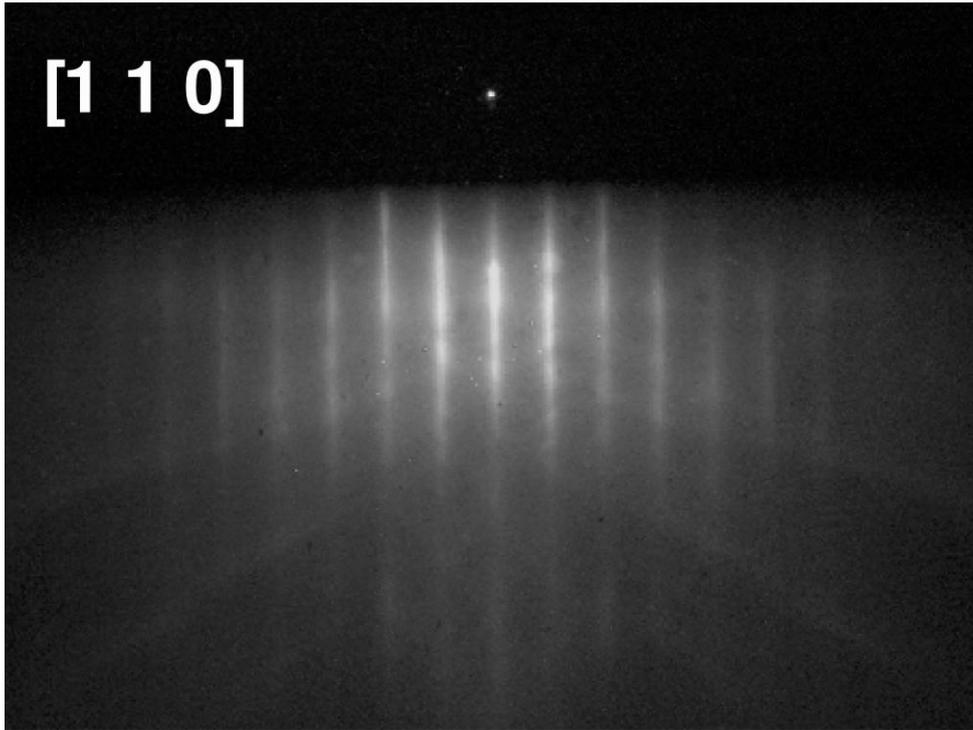


Figure 2. RHEED patterns of GaAs-S surface after vapour-deposition of {Pd}.

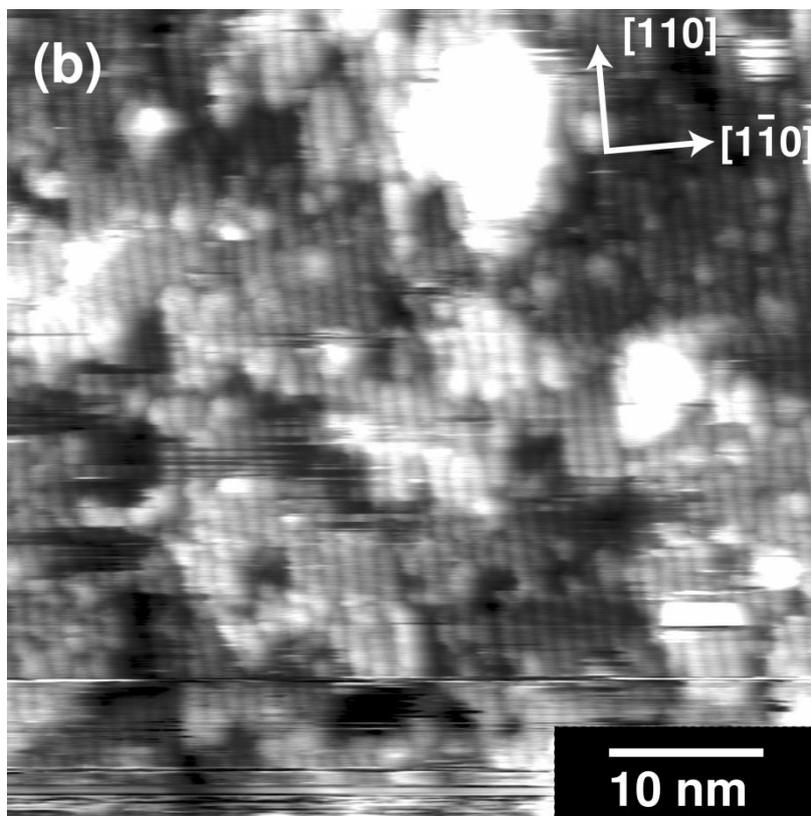
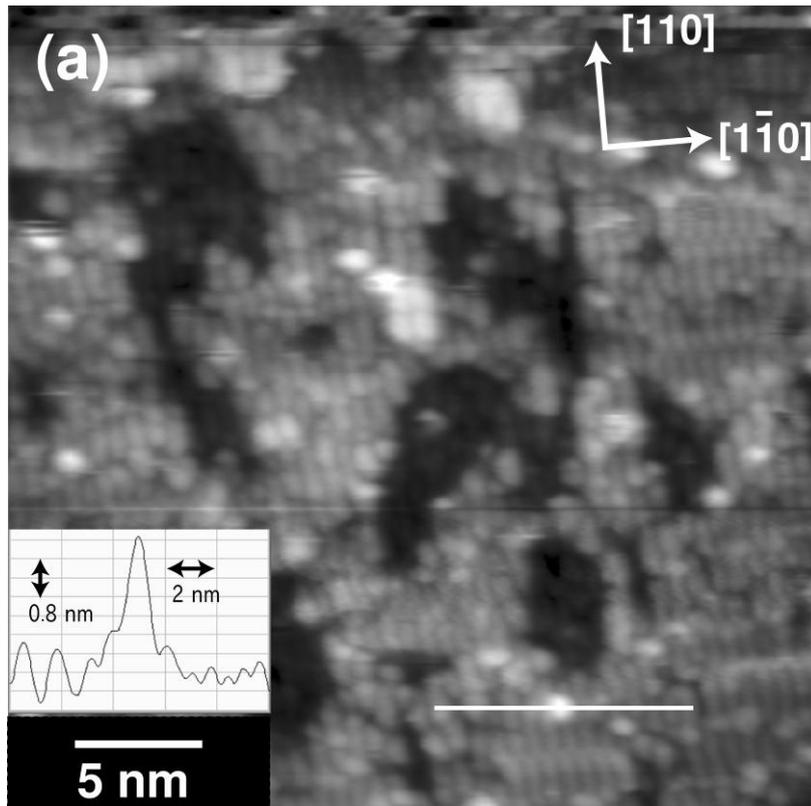


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