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Synthesis and characterization of surface oxide films on CoGa(100)

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ABSTRACT

It has been shown that a Ga_2O_3 film forms on the surface of CoGa alloy crystals when exposed to oxygen (Pan, 2001 and Vlad, 2010). In this work we report the results of the characterization of surface oxides on CoGa(100) using X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and ion scattering spectroscopy (ISS). The oxides were synthesized using either O_2 or NO_2 as the oxidant at 300 K or in excess of 700 K. ISS scans showed that cobalt was always present in the top surface layer regardless of oxidation conditions. XPS showed that depending on the oxidant and the temperature, the composition of the oxide films vary depending on oxidation treatment, with some oxides being nearly all Ga_2O_3 and ordered with a sharp LEED pattern consisting of (2×1) domains rotated by 90º and others being Co–Ga mixed oxides that gave no diffraction pattern.

1. Introduction

Oxide thin films are very useful materials due to the wide range of properties they can exhibit, which can be manipulated by changing the film thickness, underlying substrate, or surface termination [1–3]. Very thin oxide films (<5 layers) exhibit vastly different properties than the bulk, while thicker films approach the behavior of the bulk [2]. Growing these oxide films on conductive metallic substrates also allows them to be studied using conventional ion and electron spectroscopy techniques without the charging that occurs on bulk oxide crystals. Due to the lattice mismatch between the oxide film and the underlying metal substrate, these oxide films often contain point and line defects. These defects are often present in large enough quantity to influence the reactivity of the very thin oxide films [2]. Additionally, oxide thin films can be further functionalized by the deposition of metallic nanoparticles that can be used as model nanocatalysts for fundamental studies of heterogeneous reactions. These model systems can be used to study a wide variety of reactions, including alcohol synthesis, CO oxidation and CO_2 reforming [3–7].

Gallium oxide has become a material of interest both as a component of a bifunctional methanol synthesis catalyst [6,8–11], and as the basis of a material for visible light photochemistry [12–14]. The Pd/Ga_2O_3 methanol synthesis catalyst has been found to be more efficient [6] than Cu/ZnO and can use a CO_2/H_2 feed rather than syngas (CO/H_2), which is relevant to efforts for CO_2 mitigation. The powder studies, while elucidating the mechanism of the methanol synthesis reaction, do not make any attempt to characterize the catalyst. Much of the structural information related to this catalyst remains unknown. The insulating nature of the Ga_2O_3 support prevents the use of surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) to be used on a structurally well-defined gallia single crystal surface. Hence, it would be useful to be able to make a gallia thin film on a conductive substrate so that surface science techniques can be used to investigate the structure and chemical properties of the Pd/Ga_2O_3 catalyst.

Recently there have been studies indicating that oxidation of a CoGa(100) crystal results in a [010] β-Ga_2O_3 film at the surface, with oxygen exposures as low as 300 L [15–18]. The CoGa(100) substrate has been studied using thermal energy atom scattering, which determined that the surface is either Co or Ga terminated at room temperature, while Co segregates to the surface once the surface temperature reaches 850 K. The surface step height was calculated as two atomic layers, indicating that the surface termination is more stable with a single metal [19]. Structural modeling suggests that the most stable surface is Ga terminated at room temperature [20]. DFT calculations also indicate that oxidation with an O_2 pressure of 10^{-7} to 10^{-6} mbar results in a full gallium oxide monolayer due to the high density of diffusing oxygen atoms. Moreover, gallium oxide islands were predicted to grow two dimensionally, with growth being faster along the [010] direction than the [100] direction, which was then confirmed using X-ray diffraction [20]. When prepared at O_2 pressures of 10^{-8} mbar, the resultant islands have lengths of hundreds of nanometers, while their widths are in the 2–14 nm range. This growth mechanism yields gallium oxide stripes with widths of two to three unit cells [20].

Scanning tunneling microscopy and crystal rod truncation spectroscopy both show that gallium oxide forms in domains oriented at

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90º with respect to each other. These domains are readily visible in STM, and appear to form patches rather than an uninterrupted film [16]. Theoretical calculations confirm domain formation, but indicate that the gallium oxide film differs from the bulk solid because the cubic symmetry of the substrate acts as a constraint on the formation of the oxide film. Nonetheless, LEED images taken of the surface oxide show a sharp pattern consisting of two (2 × 1) domains rotated by 90° with respect to each other, indicative of an ordered surface [15]. Only when the oxygen pressure is very high (10^{-3} mbar) can the bulk β-Ga_2O_3 phase form on the CoGa(100) [17] crystal surface.

In this work, we used XPS, ISS, and LEED to characterize the extent of gallia film formation on CoGa(100) for different oxidizing conditions, including the use of NO_2 which is known to be a stronger oxidizer than O_2 under the same exposure/temperature conditions. We discovered that oxidation of the CoGa surface with O_2 or NO_2 does not form an uninterrupted oxide film, even when the surface Ga atoms are fully oxidized to Ga^{3+}. Additionally, the composition and structure of the oxide film changes depending on oxidation conditions, with evidence of patches of gallium oxide interspersed with metallic Co, or a Co–Ga mixed oxide film.

2. Experiments

Experiments were performed in a UHV chamber equipped with X-ray photoelectron spectroscopy (XPS), Ion Scattering Spectroscopy (ISS), and Low Energy Electron Diffraction (LEED) with a base pressure of 6.7×10^{-10} mbar [21]. The sample was fastened to a molybdenum plate that was spot welded to four tantalum wires serving as heating legs, allowing the sample to be heated to 900 K, with temperature monitored by a K-type thermocouple spot welded to the molybdenum plate. The CoGa(100) single crystal (Princeton Scientific) used in this study was a 1:1 alloy which had an orientation accuracy of <1° and was cleaned by repeated cycles of Ar^+ sputtering at elevated temperature (700 K). The sputtered crystal was then annealed for 1 h at 700–800 K. The clean state of the surface was confirmed by Auger electron spectroscopy and LEED. The oxide surfaces were prepared on the clean CoGa(100) surface by background dosing the oxidant gas. Both O_2 and NO_2 were used to prepare the oxide by dosing the gas at surface temperatures ≥700 K or by dosing at 300 K. Nitrogen dioxide is a more aggressive oxidant than oxygen and was used in an effort to create a complete, uninterrupted gallium oxide surface layer without any exposed substrate.

The oxide surface was characterized using XPS, ISS, and LEED to determine the effect of the oxidation treatment. Samples prepared at 300 K were annealed at 700 K for 10 min, after which it was characterized a second time. The dose of O_2 at 800 K was 5400 L in an attempt to fully oxidize the surface. The 300 K dose of O_2 was 2400 L, chosen in an attempt to recreate a previous experiment [16]. The NO_2 dose was 3240 L at 300 K, and 3600 L at 700 K. These oxidants were dosed at pressures ranging from 1.33×10^{-6} mbar to 6.65×10^{-6} mbar, with the intention of forming complete surface oxide layers.

ISS measurements were taken using a 500 eV Ne^+ ion beam at an incident angle of 45º to the surface normal. Ne^+ was used in order to maximize the separation between the Co and Ga peaks, as the masses of the two atoms are very similar, approximately 59 and 69 amu, respectively. Under these conditions, the expected energy positions for Ne^+ ions scattering off Co and Ga atoms at the surface can be calculated from the expression [22].

$$\frac{E_1}{E_0} = \left[\frac{1}{(1+A)^2}\right]\left(\cos\theta \pm \sqrt{A^2 - \sin^2\theta}\right)^2$$

where E_0 is the energy of the incident ion, E_1 is the energy of the backscattered ion, θ is the angle of the backscattered ion relative to the direction of the incident ion and A is the mass of the surface atom divided by the mass of the incident Ne^+ ion. For $E_0 = 500$ eV and $\theta = 135°$, the scattered ion energies are predicted to be 146 eV and 180 eV for Co and Ga atoms, respectively. The latter are in excellent agreement with the observed ISS spectra (see Fig. 5). An Al Kα source (1486.7 eV) positioned at 45° to the surface was employed for XPS measurements. ISS measurements were always conducted after XPS measurements in order to avoid modification of the surface by Ne^+ ion sputtering. The acquisition time for each spectrum was approximately 2 min, which was not enough time for the impinging ions to change the surface composition. XPS photoelectrons and ISS ions were collected and analyzed in a concentric hemispherical analyzer (Thermo Scientific) positioned normal to the surface with a fixed pass energy of 20 eV. XPS spectra near 20 eV (Ga 3d), 780 eV (Co $2p_{3/2}$), 530 eV (O 1s), and 1120 eV (Ga $2p_{3/2}$) were used to characterize oxidation states and atomic composition of the surface before and after oxidation. Surface oxidation by NO_2 ultimately leads to the formation of N_2 which readily desorbs from the surface except at very low temperatures (<100 K). Survey XPS scans (not shown) following surface oxidation with NO_2 did not show any discernible N 1s feature (~400 eV) above background, so the N 1s region was not explored further. The Avantage (Thermo-Fisher Scientific) software was used to fit the peaks with a Shirley background and quantify the level of oxidation. Peaks were referenced to a value of 284.1 eV for C 1s corresponding to carbon black [23]. The average value for the C 1s peak experimentally was 283.93 eV, so all adjustments to this reference were quite small. LEED patterns were acquired using a screen voltage of 4 kV and beam energy between 115 and 130 eV.

3. Results & discussion

Fig. 1 shows the LEED pattern observed when the surface oxide was formed via treatment with oxygen at 800 K. This pattern appears to be (2 × 2), but could also be ascribed to a (2 × 1) pattern with two domains rotated by 90º which would be consistent with previous work on the CoGa(100) alloy when treated with O_2 under similar conditions [15]. This LEED pattern was not observed following oxygen treatment at 300 K, but began to appear upon progressive annealing at higher temperatures. The sharpest LEED patterns formed when the oxygen was dosed at temperatures in excess of 700 K. When the surface was oxidized using background exposures of NO_2, no LEED pattern was seen. As shown below, the absence of a sharp LEED

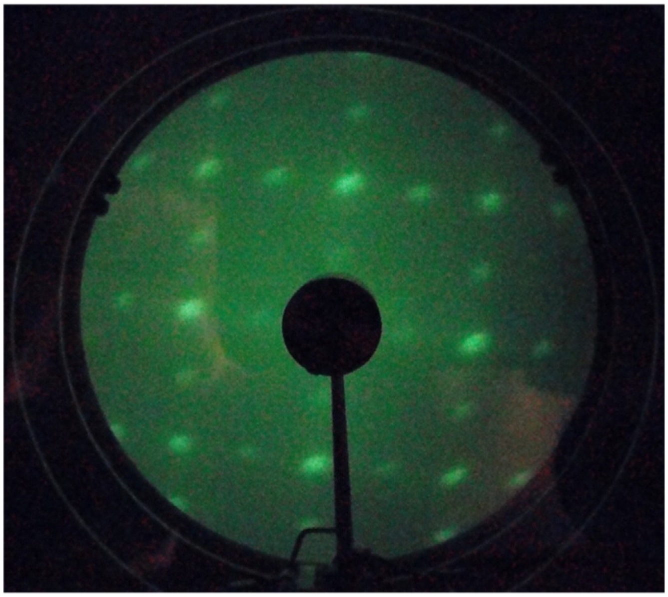

Fig. 1. LEED pattern of surface oxide formed when CoGa(100) is treated with O_2 at high temperature, in agreement with previously published work[15].