



## Structure of ultra-thin Ti film on the Al(001) surface

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### ABSTRACT

The atomic structure of sub-monolayer amounts of Ti deposited on the Al(001) surface at room temperature has been investigated using low-energy electron diffraction (LEED) and low-energy ion scattering spectroscopy (LEIS). The Ti coverage was determined using Rutherford backscattering spectroscopy (RBS). Though a crisp LEED image is inherently difficult to obtain, the symmetry of the observed  $c(2 \times 2)$  LEED images allows us to infer a structure which places Ti atoms in every other Al lattice site. Analysis of the LEIS azimuth- and polar-angle scan spectra has been done to determine the best structural model which supports the  $c(2 \times 2)$  symmetry of the LEED image as well as LEIS experimental data. It was concluded that the best model consistent with the experimental data, puts Ti preferentially below the surface of the Al substrate at every other lattice site for sub-monolayer coverage of Ti on Al(001). As Ti coverage increases, the presence of Ti atoms in the surface layer also increases. Results of this study are relevant to research pertaining to the possible use of Ti as a catalyst in sodium alanate ( $\text{NaAlH}_4$ ) in hydrogen storage applications.

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### 1. Introduction

Metal-on-metal interfaces have been studied extensively in an effort to understand the interaction between metals in alloying or their reluctance to alloy, and in epitaxial growth of deposited species. The structure of Ti on the Al(001) crystal surface however, is not well understood. Accordingly, experimental and theoretical studies have attempted to shed light on this structure. Recent interests in chemical storage of hydrogen in solid materials such as sodium alanate ( $\text{NaAlH}_4$ ) has motivated the investigation of the role of Ti as a catalyst in such applications. Kircher et al. [1] have performed experimental work with  $\text{NaAlH}_4$  doped with different concentrations of a Ti-based catalyst to study the kinetics of the decomposition of the alanate. Chaudhury et al., have added to the field of study, a theoretical treatment of Ti as a catalyst for hydrogen storage in sodium alanate [2]. Their theoretical model places Ti at next-nearest neighbor lattice sites on a quasi-hexagonal reconstructed Al(001) surface, which catalyzes hydrogen atoms to occupy spaces between Al atoms. Stumpf et al. [3] have combined experimental work and DFT calculations to study the effects of adsorbed hydrogen on the stability of Ti atoms on Al surfaces, the results of which can apply to the effectiveness of Ti as a catalyst in the absorption of hydrogen in alanate hydrogen storage media.

This work is a follow up on a previous work by our group studying the structure of Ti on the Al(001) surface [4,5]. Whereas the previous

work focused on Ti coverages up to 10 ML, this work focuses on the structural characteristics of Ti on the Al(001) surface for sub-monolayer and above but near 1 ML Ti coverage, and includes experimental results from LEED and LEIS with subsequent analysis. Previous work done by Kim et al., has suggested from partial QLEED (quantitative low-energy electron diffraction) results that low-coverage depositions of Ti onto Al(001) may find Ti atoms residing in the second layer of the substrate [6]. The work by Stumpf cited above, found similar results from their DFT calculations. Spišák and Hafner [7] proposed five theoretical models for Ti on Al(001) in a study using an ab-initio density-functional method which shows Ti atoms replacing Al atoms in their original *fcc* lattice positions in the first few top layers of the ideal Al(001) crystal surface. These five models will be considered together with the analysis of experimental LEIS spectra to assist in determining a workable surface-structure model which is consistent with experimental results.

Fig. 1 shows the five proposed models from the Spišák study [7]. All models show various configurations of one monolayer (ML) of Ti on the Al(001) surface, the most energetically preferred model being Model 5. These models will be discussed in the context of our data and a new model consistent with our results will be proposed in Section 4.

Analysis of LEIS spectra will be based on ion-target interactions under a screened-Coulomb potential [8]. Such interactions produce a shadow cone space around the target atom into which incident ions do not enter. On the surface area bounding this space, called the shadow cone boundary, a higher concentration of incident ion trajectories will be located. This is called the focusing effect. By changing the angle of the incident ion beam with respect to the sample surface, this shadow cone boundary moves in such a way as to

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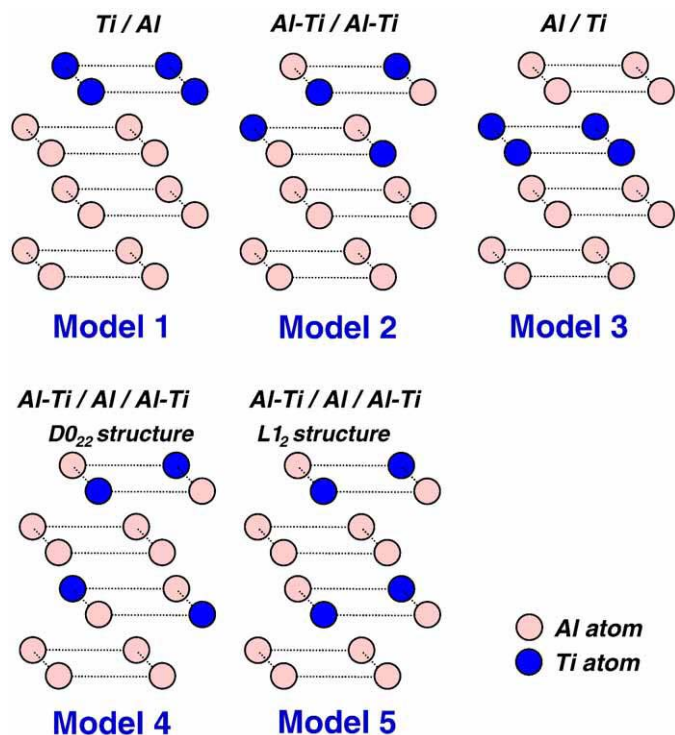


Fig. 1. Theoretical models of Ti on Al(001) proposed by Spišák and Hafner [7].

form atom interaction pairs, i.e. as the higher concentration of incident ions at the shadow cone boundary formed by the target atom, intersects another atom in the substrate, the target atom is 'paired' with this other atom in the collision process. The paired atom, called the collision atom, is located in the wake of the shadow cone boundary. Due to the focusing effect, as the shadow cone boundary intersects collision atoms, an increase in the number of detected backscattered ion counts will result, thus giving rise to corresponding peaks in collected spectra. This is the foundation of the effectiveness of LEIS azimuth- and polar-angle scan spectra in giving insight into the structural makeup of surfaces. Crucial to analysis of the resulting spectra is knowledge of the geometrical parameters of the shadow cone, such as its radius, which are functions of element type and distance from the target atom. We used a method described by Oen [9] whose work derives universal shadow cone expressions for atoms in an ion beam, to find the needed parameters. Our geometrical shadow cone analysis was based on this method to determine the possible substrate collision atoms paired with the target which could contribute to peaks found in LEIS azimuth- and polar-angle scan spectra. In contrast to RBS in which the detected backscattered ion can originate from atomic layers far beneath the surface, in LEIS the ion-neutralization probability is very high, which makes LEIS a highly surface sensitive technique [10]. Thus only the top few layers of the crystal substrate were considered in the analysis.

## 2. Experiment

Experiments were done in an ultra-high vacuum (UHV) chamber with a base pressure of  $5 \times 10^{-10}$  Torr sustained by an 8" flanged triode ion pump with a pumping speed of 220 l/s and a 6" flanged turbo pump with a pumping speed of 230 l/s. The chamber was equipped with a quadrupole residual gas analyzer, a 6" reverse-view LEED optics instrument, and an LEIS ion gun and controller with an associated 100 mm hemispherical electrostatic energy analyzer (VSW HA-100). The chamber is equipped with a high precision 3-axis goniometer for sample positioning. The sample, an Al(001) crystal, has an approxi-

mate diameter of 10 mm and is mounted in the goniometer sample holder. The sample holder also contains a resistively heated W wire filament for annealing and a Pt-resistor thermometer to monitor sample temperature, both mounted directly underneath the sample holder surface. Ti deposition onto the Al(001) crystal surface was accomplished via evaporation using a resistively heated wire filament, composed of three W wires (0.2 mm in diameter) braided together, and then wrapped with a Ti wire (0.25 mm in diameter). The chamber also has a connection through a differentially pumped beam line to a 2 MV van de Graaff accelerator, giving RBS capability for determining deposited thin-film coverage on the sample surface.

Prior to Ti deposition, the sample surface was cleaned with repeated  $\text{Ar}^+$  sputtering at an incident ion beam energy in the range 1.2–1.3 keV and current of about  $0.5 \times 10^{-6}$  A, until LEIS energy spectra showed no evidence of oxygen contamination. Following  $\text{Ar}^+$  sputter cleaning, the sample was annealed at a temperature in the range of 400–425 °C for greater than 10 min. After cooling to <50 °C, to check the condition of the Al(001) surface, LEED was performed to insure that a sharp  $p(1 \times 1)$  pattern was present. Ti deposition was carried out nominally at room temperature at chamber pressures in the range of approximately  $1\text{--}5 \times 10^{-9}$  Torr. Photographs of LEED images were taken for the clean Al(001) surface as well as for the post Ti deposited surface when a faint  $c(2 \times 2)$  image was observed.

LEIS was configured in the ion-detection mode. The scattering angle between the ion gun and analyzer was 150°. LEIS was conducted using a  $\text{He}^+$  incident ion beam at nominal energies of 1.0 or 1.2 keV and chamber  $\text{He}^+$  pressure of approximately  $5 \times 10^{-7}$  Torr. Ion currents were kept relatively low (20–30 nA) in order to minimize the damage to the sample surface which occurs from sputtering by the incident  $\text{He}^+$  ion beam.

Three types of LEIS spectra were collected, which will be called energy, azimuth-angle and polar-angle scans. Depending on instrument configuration, LEIS spectra reveal information about surface elemental composition using energy scans, and atomic surface-structure from both azimuth- and polar-angle scans. In describing the details of LEIS scans, it is helpful to define a coordinate system describing the orientation of our Al(001) crystal substrate. The sample geometry in our UHV chamber, places the plane formed by the incident ion beam from the  $\text{He}^+$  ion gun and its corresponding backscattered ion flux as it enters the electrostatic analyzer, parallel to the lab floor which we will call the horizontal plane. Referring to the experimental setup schematic shown in Fig. 2, we define the  $x$ ,  $y$  and  $z$

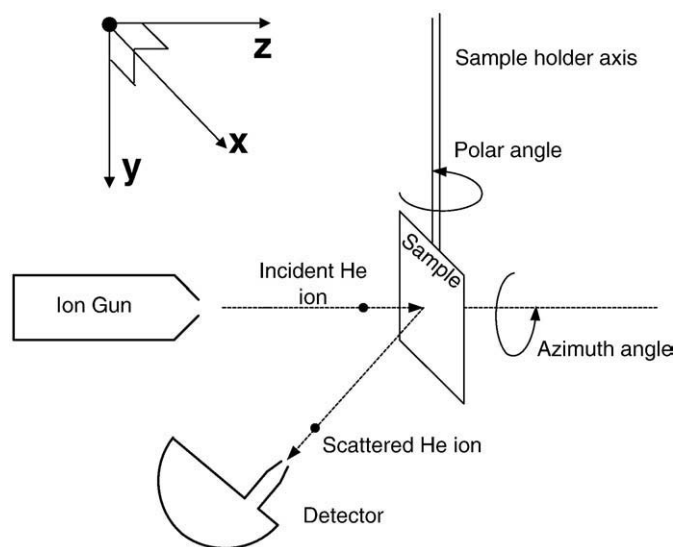


Fig. 2. Schematic of LEIS setup.

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