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ScienceDirect
Surface Science 602 (2008) 67–76
SURFACE SCIENCE
www.elsevier.com/locate/susc

Formation of a well-ordered ultrathin aluminum oxide film on Ni(1 1 1): Determination of its thickness, composition and structure

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Received 28 July 2007; accepted for publication 27 September 2007
Available online 6 October 2007

Abstract

A well-ordered ultrathin alumina film on top of Ni(1 1 1) has been obtained by an oxidation at 300 K of a thin $Ni_3Al(1\,1\,1)$ layer epitaxially grown on Ni(1 1 1) and subsequent annealing at 1000 K. The formation of this film was studied by Rutherford backscattering spectrometry (RBS) under channeling conditions, nuclear reaction analysis (NRA), Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The absolute amounts of both types of atoms participating to the oxide film are, respectively, $(2.3 \pm 0.3) \times 10^{15}$ Al/cm^2 and $(3.3 \pm 0.3) \times 10^{15}$ O/cm^2. Hence it appears that this film, with a stoichiometry very close to Al_2O_3, has an oxygen content corresponding nearly to two compact planes of oxygen in bulk crystalline alumina (about 3.0×10^{15} O/cm^2). A commensurate $(5\sqrt{3} \times 5\sqrt{3})R30°$ superstructure with a lattice parameter of 2.16 nm, can be deduced from the LEED pattern. This superstructure differs from the one observed by other authors for alumina films (of similar thickness and composition) formed on bulk-$Ni_3Al(1\,1\,1)$, a surface with symmetries and interatomic distances comparable to that of Ni(1 1 1). This difference in structure is most probably connected to the absence, in our case, of any Al atom not strongly bound to O atoms at the interface between the ordered alumina film and the Ni substrate: the Al atoms not involved in the oxide film have diffused deeply in the bulk of the Ni substrate during the high temperature annealing stage needed for alumina ordering.

Keywords: Nickel; Ultrathin aluminum oxide; Epitaxy; Superstructure; Rutherford backscattering spectrometry (RBS); Nuclear reaction analysis (NRA); Auger electron spectroscopy (AES); Low energy diffraction (LEED)

1. Introduction

Several interests, both fundamental and technological, can be found in the study of thin oxide films formed on metallic substrates, and particularly in well-ordered ultrathin oxide films on metal or metal alloy surfaces obtained, on single crystals, by high temperature oxidation [1,2]. The stoichiometry and some features of the atomic and electronic structures observed for such films may differ from those existing in the near surface region of massive oxides. This is both due to the small thickness of the films and to the interaction with the crystalline metallic substrate. These features can be studied by methods needing charge transport, like scanning tunneling microscopy (STM) or spectroscopy (STS) or other ones involving electrons or ion beams, impossible to perform on massive insulating oxides. One may be interested either in the oxide film itself, and by the way its properties depend on its thickness, or in its potential applications. In particular, such films can be used as a support for metallic atoms or clusters [3]. A two-dimensional (2D) ordering of the metallic deposits can be obtained via different mechanisms, as illustrated by two recent studies. In the first one, Au atoms deposited at low temperature on a few monolayers thin MgO film formed on Ag(0 0 1) present a 2D short range order, due to their electrostatic repulsion, after a charge transfer from

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doi:10.1016/j.susc.2007.09.050

the substrate, through the oxide [4]. In the second one, bimetallic Au–Pd clusters, nucleated on particular sites of the superstructure of an ultrathin alumina film formed on $Ni_3Al(1\,1\,1)$, present a good 2D long range order [5]. Such a regular nucleation of supported clusters, which are often observed to present an epitaxial relationship with the oxide film, tends to narrow, during their growth, their distributions in size and shape. This can be useful for several applications, e.g., in catalysis or magnetic devices.

In particular, well-ordered ultrathin aluminum oxide films formed on massive NiAl or Ni_3Al single crystals of various orientations have been the subject of many studies [2]. These films are generally obtained by an oxidation at an oxygen pressure of at most 10^{-5} mbar and around 1000 K. This high temperature treatment is made possible by the high melting temperatures of the NiAl or Ni_3Al ordered alloys (respectively, 1911 and 1658 K). We list here the general features presented by these films, on which most authors agree, even if their assumptions are not always fully demonstrated: (i) they are composed exclusively of Al and O atoms; (ii) their stoichiometry is close to Al_2O_3. In what follows we shall then refer to "alumina" films even if it is not strictly Al_2O_3; (iii) the surface of these oxide films seems to be O terminated; (iv) as long as the oxidation is achieved under low oxygen pressure the alumina films formed have a self-limited thickness, always about 5 Å, whatever is the precise oxidation procedure, with an overall oxygen content corresponding to about two compact planes of oxygen in bulk alumina.

One may remark that this self-limited thickness appears to be too small for uses of such alumina film as insulating barriers in magnetic tunnel junctions. In junctions having Ni or $Ni_{80}Fe_{20}$ (permalloy) as one of the ferromagnetic electrodes the thickness of the alumina insulating barrier is at least 1.4 nm [6,7].

Apart from their similarities in composition and thickness it has to be noticed that all the various structures observed on ultrathin alumina films formed on single crystals of massive Ni–Al alloys differ from the numerous surface structures, reconstructed or not, observed on a massive alumina single crystal of any structure (α, κ, γ, δ or θ). This is not surprising as the thicknesses of the films are markedly smaller than the size, in a direction perpendicular to compact O planes, of the unit mesh for any of the bulk structures of alumina (in corundum, this size is about 1.30 nm, corresponding to six (0 0 0 1) oxygen planes). For such a small thickness the structure and, probably to a smaller extent, the precise overall stoichiometry of the alumina film are obviously greatly influenced both by the bulk characteristics of the Al–Ni alloy used and by the orientation of its surface.

Up to now the most studied ultrathin aluminum oxide films have been formed either on massive NiAl(1 1 0) or on $Ni_3Al(1\,1\,1)$ substrates. In the former case a complex structure has to be expected, due to the rectangular surface symmetry of the substrate, to be compared to the triangular symmetry of the compact O planes. A model of this atomic structure has been recently proposed, following a combination of extensive ab initio calculations and STM observations ([8,9] and references therein). In the latter case, where the surface symmetries of the $Ni_3Al(1\,1\,1)$ substrate and of the compact O planes are both triangular, one could expect a simpler structure. In fact this structure, studied by several techniques, appears to be also complex and is not yet fully resolved at the atomic level [10–16]. The most recent studies, performed, respectively, by low temperature STM and spot profile analysis low energy electron diffraction (SPA-LEED) [15] and by dynamic scanning force microscopy (SFM) [16], concluded to an ultrathin alumina film made of two domains (rotated by 24°) of a "true" hexagonal superstructure, with a unit cell, (lattice constant of about 4.15 nm), having a $(\sqrt{67}\times\sqrt{67})$R47.784° relation to the $Ni_3Al(1\,1\,1)$ lattice. The film is terminated by a distorted hexagonal lattice of oxygen atoms (ions) rotated by 30° with respect to the substrate lattice. In this surface plane the mean distance between nearest neighbours oxygen atoms is 2.93 Å, to be compared to 2.80 or 2.75 Å, the corresponding distances in compact oxygen planes, respectively, in γ and α massive alumina.

It would of course be interesting to obtain thin epitaxial layers of Al oxide on another metallic substrate than a Ni–Al alloy. A way to achieve this goal is to start from a thin Ni–Al alloy formed on a Ni single crystal. Recent studies have shown that such alloyed layers can be prepared with good crystalline order after a proper annealing and dissolve in the Ni substrate at higher temperatures [17–19]. One may then think to oxidize the near surface region of the thin alloyed layer at low temperatures, and to dissolve the remaining alloy by high temperature annealing, obtaining hence an Al oxide on top of the Ni substrate. To our knowledge the only attempt for doing so is reported in Ref. [17], describing the growth and oxidation of a $Ni_3Al(1\,0\,0)$ layer on Ni(1 0 0) (square symmetries). After an annealing at 1200 K the so obtained oxide film was (8 ± 2) Å thick, with a hexagonal structure (two-domains) having a lattice constant 2.87 Å, that is the distance between two adjacent oxygen atoms in the (1 1 1) plane of γ′ alumina. This plane was found to be parallel to the (1 0 0) surface of the Ni substrate.

In this paper we report on the preparation and characterization of a well-ordered ultrathin aluminum oxide film on Ni(1 1 1). This film has been obtained after the oxidation around 300 K of a very thin $Ni_3Al(1\,1\,1)$ layer epitaxially grown on Ni(1 1 1) and a subsequent annealing at 1000 K. The procedure used in order to obtain the epitaxial $Ni_3Al(1\,1\,1)$ layer, starting from ultrathin Al deposits on a Ni(1 1 1) substrate, the characterization and the study of the thermal stability of the alloy formed are reported in details in Refs. [18,19]. The surface symmetries of the Ni(1 1 1) substrate and of the $Ni_3Al(1\,1\,1)$ layer being triangular, we could expect to obtain an aluminum oxide film of simpler atomic structure than the one found in Ref. [17]. One of our main aims was to compare the alumina films that we