EPITAXIAL FILM GROWTH OF SINGLE CRYSTAL Ce/V PREPARED BY MOLECULAR-BEAM EPITAXY

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ABSTRACT

The growth of epitaxial films of cerium (Ce)/vanadium (V)/on single crystal sapphires (α-Al_2O_3) was studied by in-situ reflection high energy electron diffraction and x-ray scattering. For the first time Ce(111) single crystal film was grown on V(110)/α-Al_2O_3(11$\bar{2}$0) in the Frank-van der Merwe mode. A new epitaxial orientation, different from the well known Nishiyama-Wasserman or Kurdjumov-Sachs orientations is found in the present study. Subsequent V(110) layers grow epitaxially with three equivalent domains.

I. INTRODUCTION

The growth of single crystal metal-metal epitaxial films is of current interest for the study of novel surface and interfacial phenomena [1], and to test theoretical ideas in low dimensional physics [2].

Problems such as the adsorption of rare-gas monolayers on graphite [3], the growth of fcc(111)/bcc(110) epitaxial films [4], two-dimensional melting with novel intermediate hexatic phases [5], commensurate-incommensurate phase transitions [6], orientation epitaxy [7] in rare gas/graphite systems and epitaxial layered growth [8] have been studied over a number of years. In particular, in fcc(111)-bcc(110) epitaxy it was shown that only two epitaxial orientations are allowed and observed, the so-called Nishiyama-Wasserman (NW) and Kurdjumov-Sachs orientations [4,9,10]. While there have been many studies in this respect, very little is known as yet concerning the film growth and epitaxial arrangement of immiscible metallic binary systems [11] with large mismatch.

In the present study we have used molecular beam epitaxy (MBE) to grow films, and in-situ reflection high-energy electron diffraction (RHEED) and x-ray diffraction for structural studies of the transition metal (bcc)/rare earth (fcc) system, vanadium (V)/cerium (Ce), on single crystal sapphire (α-Al_2O_3) substrates. For the first time Ce(111) single crystal films were successfully grown on V(110)/α-Al_2O_3(11$\bar{2}$0) in the Frank-van der Merwe (FM) mode [8]. In this case, the epitaxial arrangement was found to be different from the ordinary NW or KS orientations. Subsequent deposition of V(110) results in epitaxial growth with three equivalent domains separated by 120 degrees.

II. EXPERIMENTAL

The films were prepared in a Riber metal deposition MBE system equipped with in-situ RHEED and a typical base pressure of 4×10^{-11} torr. 99.9% V and 99.99% Ce (Johnson Matthey Inc.) were evaporated at a rate of 0.5-1.0 Å/sec in a vacuum better than 2×10^{-10} torr on temperature controlled (300-1000 C)

substrates. 10 keV RHEED was used to evaluate the surface roughness and morphology of deposited films and substrate. Further detailed measurements of epitaxial arrangements and lattice constants were carried out using the precession camera technique [12] with Mo-Kα line and a computer-controlled Rigaku DMaxII two-circle x-ray diffractometer using 2kW Cu-K_α radiation, after removal of the sample from the MBE system.

a) V(110) growth on α-$Al_2O_3(11\bar{2}0)$

Single crystal V(110) films were grown on temperature controlled $(11\bar{2}0)$ single crystal sapphire substrates. Figure 1 shows the RHEED patterns at two different V film thicknesses grown at 900°C, d_V = 11 Å and 1000 Å, at two different vanadium azimuthal direction $[\bar{1}1\bar{1}]_V$ and $[\bar{1}10]_V$. The initial V films grow in island-like (Volmer-Weber, VW) mode (Fig. 1 (a) and (b)) showing three-dimensional spotty diffraction patterns. However, around $d_V \cong 30$ Å streaks start to develop indicating smooth two-dimensional growth as shown for a 1000 Å V film (Fig. 1 (c) and (d)). At substrate temperatures (T_S) below ~600°C, the V film growth becomes polycrystalline. The diffraction spots and streaks, perpendicular to the incident electron beam give lattice constants which are close to the bulk bcc V value in both the perpendicular and in-plane directions (a_0 = 3.0274 Å). The orientation of the V(110) film on α-Al_2O_3 $(11\bar{2}0)$ is found to be $(110)_V/(11\bar{2}0)$ α-Al_2O_3

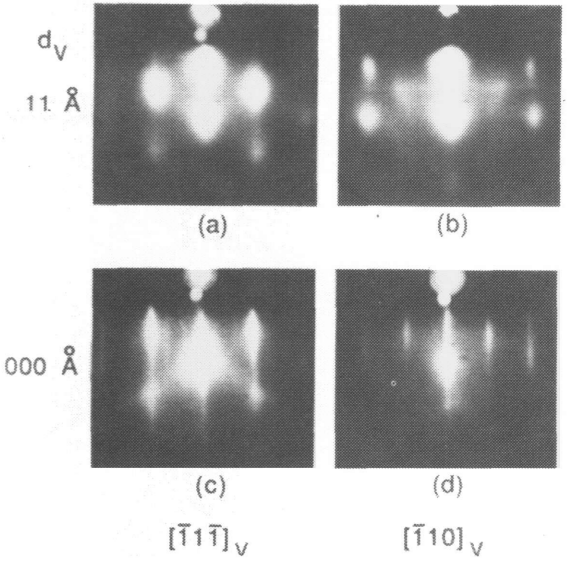

Fig. 1. RHEED patterns of V(110) films on α-Al_2O_3 $(11\bar{2}0)$ for d_V = 11 Å ((a) and (b)) and d_V = 1000 Å ((c) and (d)) film thickness. The azimuthal directions are $[\bar{1}1\bar{1}]_V$((a) and (c)) and $[\bar{1}10]_V$ ((b) and (d)).

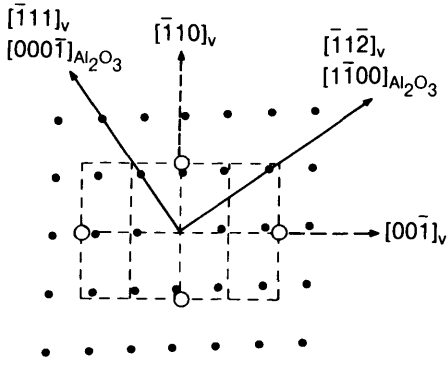

Fig. 2. Precession camera photograph of 1000 Å V(1210)/α-Al_2O_3 (11$\bar{2}$0). The incident X-ray beam is normal to the film plane. The indexed crystallographic orientations are consistent with the RHEED results.

with [$\bar{1}$11]$_v$//[0001]α-Al_2O_3 and [$\bar{1}$1$\bar{2}$]$_v$//[1$\bar{1}$00]α-Al_2O_3, as determined from the RHEED analysis and also the Buerger-precession camera technique (see Fig. 2) The sapphire indexing is based on the crystal symmetry (R$\bar{3}$c) with a hexagonal lattice constants a_o^h = 4.7593 Å and c_o^h = 12.9912 Å [13]. The same epitaxial configuration was observed in the Nb(110)/α-Al_2O_3 (11$\bar{2}$0) system [11,14].

b) Ce(111) Growth on V(110) Layers

The element Ce is a promising candidate for interesting epitaxial behavior since it exhibits a variety of structural phases as a function of temperature and pressure [15]. The binary phase diagram of Ce and V shows them to be immiscible, without any solid solution being present [16].

The Ce films were deposited on 1000 Å single crystal V(110) film at $T_s \approx 350°C$. The unexpected findings of our studies are that from the very beginning Ce(111) grows epitaxially in layer-by-layer (FM) mode on the V(110), and that the epitaxial arrangement of Ce(111) on the V(110) is neither of the much studied NW or KS configurations. Figure 3 shows the RHEED patterns of a 3 Å and a 50 Å Ce(111) films at two different azimuths [1$\bar{2}$1] (Fig. 3 (a) and (c)) and [0$\bar{1}$1] (Fig. 3 (b) and (d)). The narrow, equally spaced streaks indicate that the surface is two-dimensional and single crystal. The RHEED line spacing implies that the Ce(111) inplane lattice constant is compressed by ~ 8% relative to the bulk value of γ-Ce (a_o^{Ce} = 5.1610) [17]. The epitaxy of Ce on V as determined from RHEED analysis, shows that Ce [0$\bar{1}$1] is parallel to V [$\bar{1}$10]. This has never been observed before in any fcc(111)/bcc(110) system and is different from either the KS ([0$\bar{1}$1]$_{fcc}$//[1$\bar{1}$1]$_{bcc}$) or NW ([0$\bar{1}$1]$_{fcc}$//[001]$_{bcc}$) orientations. The atomic arrangement is illustrated in Fig. 4 together with the KS and NW cases.

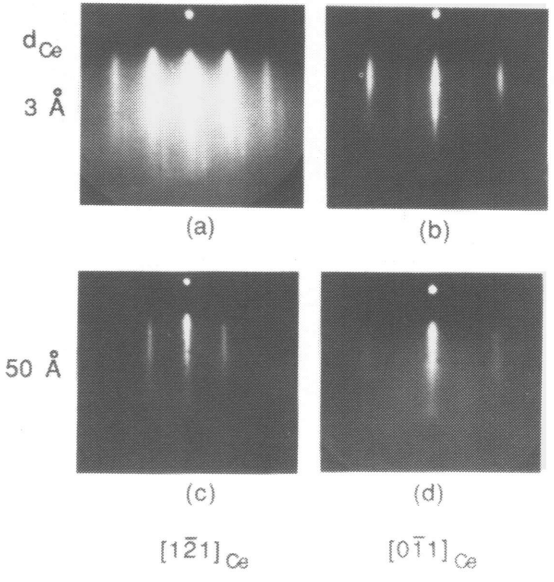

Fig. 3. RHEED patterns of Ce(111) on V(110) films for d_{Ce} = 3 Å ((a) and (b)) and d_{Ce} = 50 Å ((c) and (d)) thicknesses. The azimuthal directions are $[1\bar{2}1]_{Ce}$ ((a) and (c)), and $[0\bar{1}1]_{Ce}$ ((b) and (d)).

Bruce and Jaeger's [9] epitaxial studies in electron microscopy experiments and Moire fringe simulation shows that the ratio of the bulk atomic diameters $\rho = d_o(bcc)/d_o(fcc)$ determines whether KS or NW orientation is present (KS for $0.89 < \rho < 1.01$, and NW in the range $0.82 < \rho < 0.87$ and $1.03 < \rho < 1.15$). The value of ρ in the V(bcc)/Ce(fcc) is $\rho = 0.72$ which is out of their range of consideration. The fcc(111)/bcc(110) epitaxy has been studied by van der Merwe [10] using an elastic model and by Ramirez et al. [4] using a rigid model and molecular dynamics. Both studies confirmed the results of Bruce and Jaeger [9]. It should be stressed that the KS and NW orientation only differ by ~5° so they are almost impossible to distinguish using a qualitative tool such as RHEED. The new epitaxial configuration found here, in the largely mismatched V/Ce system, suggests that other factors besides ρ and bonding strengths are important for an epitaxial configuration, for example, electronic structure (perhaps 4f electron hybridization at the interfaces).

Additional X-ray diffraction studies of V(100 Å)/Ce(100 Å)/V(1000 Å)/α-Al_2O_3 $(11\bar{2}0)$ samples show that the Ce(111) lattice spacing is close to the γ-Ce(111) value of d^{Ce}_{111} = 2.98 Å with a mosaic spread $\Delta\omega \sim 0.4°$, and that $d^{V}_{110} \sim 2.14$ Å with $\Delta\omega \sim 0.15°$ which is comparable to the α-Al_2O_3 $(11\bar{2}0)$ mosaic spread. The Ce layer retains the γ-phase atomic spacing along <111> although as shown above the in-plane lattice spacing contracts ~8%. On the

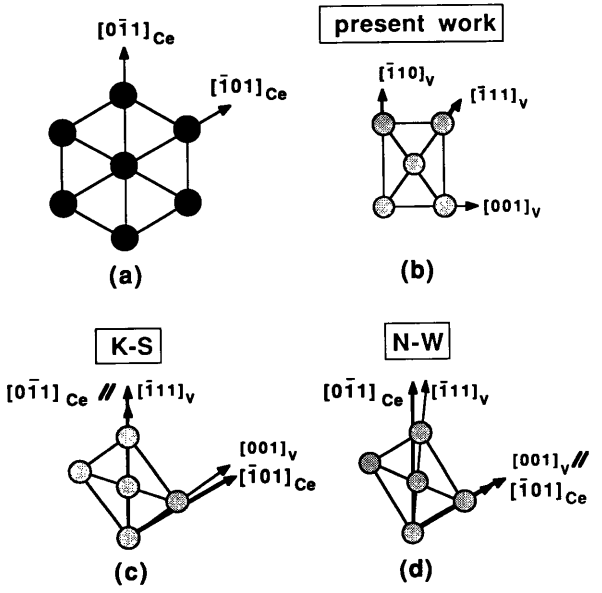

Fig. 4. Epitaxial arrangement of Ce(111) on V(110). (a) Atomic arrangement of the Ce(111) plane (b)-(d) orientation of the V(110) plane with respect to the Ce(111) plane, (b) the new configuration $[\bar{1}10]_V//[0\bar{1}1]_{Ce}$, (c) K-S configuration $[\bar{1}11]_V//[0\bar{1}1]_{Ce}$, and (d) N-W configuration $[001]_V//[0\bar{1}1]_{Ce}$.

other hand, the V (110) film essentially has the same structure as bulk V.

In order to explore the feasibility of growing single crystal superlattices V(110) was grown on a single crystal Ce(111)/V(110)/α-Al_2O_3 (11$\bar{2}$0) combination. In this case, the V growth was quite different from the structure obtained when grown directly on the α-Al_2O_3 (section IIa). Although a variety of substrate temperatures up to T_s = 600 C were explored, the growth was always VW (spotty pattern). The RHEED analysis indicates that there are three equivalent domains separated by 120°. Clearly further studies including higher temperature studies are needed to explore the possibility of growing atomically smooth V on single crystal Ce. The combination of Ce showing valence-fluctuations and Kondo effect [18] with the superconducting V [19] will provide us a new opportunity to study current problems such as the physics of heavy electron systems [20].

In conclusion, epitaxial film growth of Ce/V on α-Al_2O_3 (11$\bar{2}$0) has been studied by in-situ RHEED and x-ray scattering. For the first time Ce(111) single crystal films were grown on V(110) in the Frank-van der Merwe mode. The epitaxial arrangement was found to be different from the well-known Nishiyama-Wasserman and Kurdjumov-Sachs orientations. This may indicate that the electronic structure at the interface plays an important role in the Ce/V system.

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