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Epitaxial refractory-metal buffer layers with a chemical gradient for adjustable lattice parameter and controlled chemical interface

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We have developed and characterized the structure and composition of nanometers-thick solid-solution epitaxial layers of (V,Nb) on sapphire (11 $\bar{2}$ 0), displaying a continuous lateral gradient of composition from one to another pure element. Further covered with an ultrathin pseudomorphic layer of W, these provide a template for the fast combinatorial investigation of any growth or physical property depending of strain.

Thin films play a crucial role in integrated technology and it is necessary to control their physical properties. In a down-scaling approach one seeks to sustain the bulk properties. One may also endeavor to tailor new properties that do not occur in the bulk, an approach being one basis for the development of nanosciences. The parameter often at play in the change of properties in thin films is strain¹, influencing *e.g.* mobility in semiconductors², optical activity, electric polarization or magnetic moment³ and anisotropy⁴. The easiest way to control strain in thin film is through their epitaxy on substrates with a lattice parameter different from their own, inducing a so-called lattice misfit. Lattice misfit also influences growth modes (smooth or rough films, islands...)^{5,6}, which strengthens the need for its control.

Effects of lattice misfit are often investigated by growth on single crystals of various pure elements, each with a well-defined lattice parameter. Alloys and solid solutions (s.s.) are an appealing combinatorial alternative as they allow for the continuous control of lattice misfit, which is not possible for pure elements⁷. Nevertheless, systematic studies with s.s. require several samples with different compositions, with issues of time, reproducibility and limited number of data points. To circumvent this Kennedy *et al.*⁸ have introduced compositional spreads, where the anisotropy of evaporation of two sources are used to create a slight gradient of composition across a sample. Later, alternated deposition of the materials along with moving masks were used to create intercalated wedges of two or three elements^{9,10}. This allows one to vary the composition linearly and potentially from 0% up to 100%. In these seminal uses of masks the alloy resulted from a post-annealing, which is not suited for most epitaxial and thin films. Only Zhong *et al.* applied this technique to epitaxial materials (semiconductors), however restricted it to the case of weak doping¹¹.

We issued a preliminary report of chemical gradients with controlled chemical surface¹², however with a neg-

ligible variation of lattice parameter via mixing body-centered cubic (bcc) Mo (lattice parameter 3.157 Å) and W (3.165 Å), therefore with virtually no metallurgical issues and with restricted practical use. Here we report the fabrication, the structural, composition and surface characterization of epitaxial Chemical-Gradient Layers (CGLs) of bcc refractory metals, in the full range of composition to adjust the lattice parameter over 10%. Further combined with an ultrathin pseudomorphic layer, these provide a versatile buffer-layer toolkit for the elucidation and use of the many phenomena depending on lattice mismatch.

The samples were grown using Pulsed-Laser Deposition in a set of Ultra-High-Vacuum chambers. The laser is a 10 Hz-pulsed Nd-YAG laser with pulse length \approx 10 ns and doubled frequency ($\lambda = 532$ nm). The deposition chamber is equipped with a computer-controlled mask moving in front of the sample, and 10 kV Reflection High Energy Electron Diffraction (RHEED)¹². Our CGLs are based on mixtures of two bcc elements (Mo, W, Nb, V), that all form s.s. one with another. Results are illustrated in this Letter with the case of (V,Nb). (11 $\bar{2}$ 0) sapphire wafers are used as a support, resulting in the (110) texture of the films^{12,13}. Searching for an optimized procedure, CGLs were grown directly on 0.7 nm-thick-Mo-dusted sapphire wafer (Mo is inserted to avoid crystallographic variants¹²), or on an atomically-flat 10 nm-thick W(110) buffer layer itself above Mo-dusted sapphire. The wedges of the two elements are deposited sequentially, in an opposite fashion thanks to the azimuthal rotation of the sample of 180°. The length of the wedges is 5 mm (FIG. 1a). Their typical thickness is 1 Å, which is less than one atomic layer, with a view to promote the mixture of both elements at the atomic level and avoid the formation of misfit dislocations that would occur for thick individual layers. Deposition is performed at moderate temperature (300 °C), followed by annealing for 30 min at 800 °C to smoothen the surface. The typical total thickness of these films is 10 nm.

FIG. 1 shows RHEED patterns and Scanning Tunneling Microscopy (STM) images of a (V,Nb)/Mo(0.7 nm) CGL directly grown on sapphire. The RHEED streak

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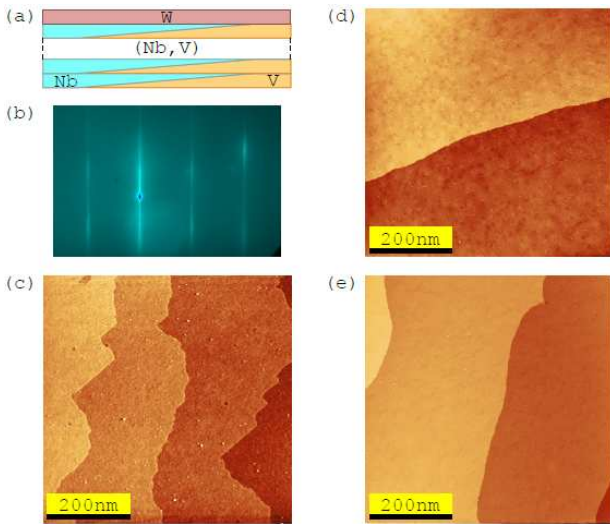


FIG. 1. (a) Schematics of a CGL, further covered by an ultrathin W layer for the chemical control of the free surface. (b) typical RHEED pattern, for electron azimuth $[1\bar{1}0]$ (the bright spot is the reflected beam). STM images of (V,Nb)/Mo(0.7 nm)/Al₂O₃ CGLs (not covered with an ultrathin W layer) for (c) V, (d) V₅₀Nb₅₀ and (e) Nb .

1 narrowness, large terrace size and absence of emerging
 2 screw dislocations, provide a picture of a high-quality
 3 crystal. No significant difference is found in RHEED and
 4 STM data as a function of the local composition, from
 5 pure V to pure Nb, with or without an underlying W
 6 buffer layer.

7 We developed a sample holder to perform X-Ray
 8 Diffraction over a small and precise location on the
 9 sample. It consists of a 1 mm-wide window between
 10 two steel blades machined at an angle of 12° to let
 11 in and out X-rays down to grazing incidence. The
 12 blades are covered with a 10 μm-thick layer of metallic
 13 glass (Zr_{52.5}Ti_{2.5}Cu₂₂Ni₁₃Al₁₀) to avoid diffraction from
 14 the mask. A manual sample translator allows one to se-
 15 lect the area of investigation (inset of FIG. 2a). FIG. 2a
 16 shows $\theta - 2\theta$ spectra as a function of location on the sam-
 17 ple, translated into the expected composition. The oc-
 18 currence of Kiessig fringes arises from the finite thickness
 19 of the films and the absence of roughness. Their width
 20 is composition-independent and consistent with the film
 21 thickness. The films are thus coherent across their entire
 22 thickness, showing their good layered structure, consis-
 23 tent with STM data (FIG. 1c-e). The out-of-plane lat-
 24 tice parameters extracted from these curves are shown
 25 in FIG. 2b. The error bars result from the precision of
 26 the lateral position of the sample, and from the com-
 27 bined fitting of peaks and calibration of the diffractome-
 28 ter against the first and second order peaks of sapphire.
 29 Within the error bar the lattice parameter varies linearly
 30 with composition and ranges from the bulk lattice pa-
 31 rameter of V (3.02 Å) to that of Nb (3.30 Å), in agree-
 32 ment with Vegard's Law. *in situ* RHEED yields the in-

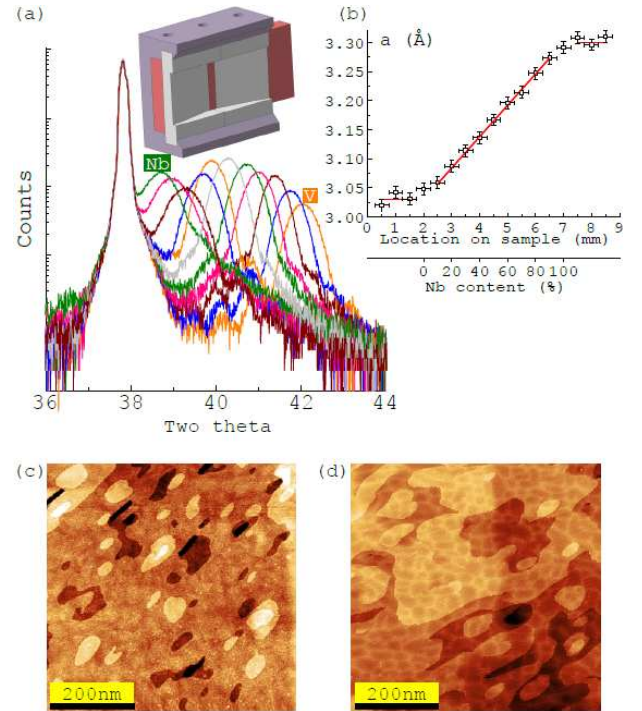


FIG. 2. (a) $\theta - 2\theta$ diffraction spectra of (V,Nb)/Mo(0.7 nm)/Al₂O₃ CGLs. At 37.85° is a sapphire peak. Inset: mask used to select the area of interest for diffraction (b) Extracted from (a), out-of-plane lattice parameter as a function of composition along the CGL. Lines are the expectation of Vegard's law. STM images of ultrathin layers of W of thickness (c) 0.6 nm and (d) 2 nm on a CGL.

plane lattice parameter, albeit with larger error bars (not shown here). These also fit Vegard's law, demonstrating the good structural relaxation of the s.s.. Finally, the CGLs may be covered by an ultrathin W layer deposited at 250 °C and then annealed at 800 °C, a procedure known not to give rise to intermixing with the underlying film¹². STM shows that W remains pseudomorphic up to ≈ 1 nm (FIG. 2c), above which relaxation is revealed by an array of misfit dislocations (FIG. 2d)¹⁴. CGLs covered with this ultrathin pseudomorphic W layer provide a surface with a continuously-variable lattice parameter, however with a uniform and a rather inert surface material.

In order to check locally both the composition of the s.s., and their crystalline quality, the samples were also analyzed using Rutherford Backscattering Spectrometry (RBS) both in random and channeling geometries (for these analytical techniques, see Ref.¹⁵). Indeed, whereas X-ray and electron diffraction probe long-range crystalline coherence and are mostly insensitive to local disorder, RBS in a channeling geometry is highly sensitive to such disorder and is thus very valuable to refine the close-to-perfect picture of CGLs given by FIG. 1 and 2. RBS was performed within the SAFIR facility of the INSP, using a 1.4 MeV ⁴He⁺ ion beam with a 0.5 mm diameter,

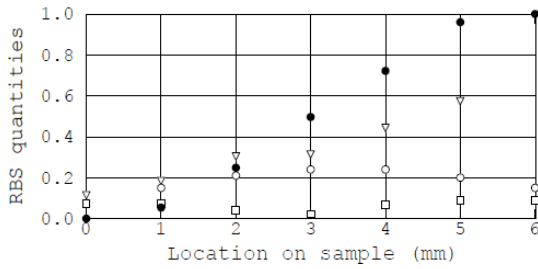


FIG. 3. Local quantities determined by RBS (random or channeling conditions), as a function of the location x across a (V,Nb)/W(10 nm)/Mo(0.7 nm)/Al₂O₃ CGL: Nb concentration (●), normalized channeling ([110] alignment) yields Y_{Nb} (○), Y_V (▽) and Y_W (□) (see text). The zero for the lateral scale is different from that of FIG. 2b.

1 produced by a 2.5 MV Van de Graaff accelerator. The 54
 2 ions scattered elastically at large angle (here $\approx 150^\circ$) on 55
 3 the sample nuclei (rare scattering events) were energy- 56
 4 analyzed using a silicon detector. 57

5 Conversely, the most probable scattering events result 58
 6 in small-angle repulsive deflections. When the incident 59
 7 beam is aligned with a major crystallographic axis of 60
 8 a crystal (channeling geometry, here performed along 61
 9 [110]), these deflections are correlated and the particle 62
 10 flux close to the rows is strongly reduced, leading to a
 11 similar reduction of the RBS yield Y with respect to the
 12 yield R using a random orientation of the beam. For 63
 13 convenience, in the following Y values are normalized to
 14 the corresponding RBS random yield. Whereas R_i values
 15 for element i are proportional to the absolute amount 64
 16 of i atoms in the layer, Y_i values are mostly sensitive to
 17 atomic displacements in the plane perpendicular to the 65
 18 channeling axis¹⁶. 66

19 Various samples were analyzed, but we only present 69
 20 here the case of (V,Nb) deposited on a 10 nm-thick 70
 21 W(110) buffer layer (FIG. 3). Both $R_V(x)$ and $R_{Nb}(x)$ 71
 22 exhibit a linear variation across the sample, their sum 72
 23 keeping a nearly constant value corresponding to a thick- 73
 24 ness of about 10 nm of the (Nb,V) layer. This provides a 74
 25 direct quantitative confirmation of the linear variation of 76
 26 composition [*e.g.* $C_{Nb} = R_{Nb}/(R_{Nb} + R_V)$] with x , sug- 77
 27 gested indirectly previously through the agreement with 78
 28 Vegard's Law (FIG. 2). 79

29 Concerning the crystalline quality of the s.s., the rela- 81
 30 tively high channeling yields Y_{Nb} and Y_V observed on 82
 31 FIG. 3, with a marked dependence on C_{Nb} , may hint at 83
 32 atomic displacements in the s.s., relatively far from the 84
 33 CGL-W interface (see below). Their precise identifica- 85
 34 tion needs further analysis. Despite this, paradoxically, 86
 35 the very low channeling yield Y_W in the range [0.02–0.05] 87
 36 is indicative of a very good epitaxy. The highest qual- 88
 37 ity ($Y_W \approx 0.02$) is obtained for Nb_{0.5}V_{0.5}, for which there 89
 38 is no lattice mismatch between the alloy and W, in agree- 90
 39 ment with FIG. 2b. 91

40 To conclude, we developed high-quality epitaxial solid- 94

41 solution layers of refractory metals along the orientation
 42 (110), in the form of Chemical-Gradient Layers (CGLs).
 43 These CGLs were then covered with a flat and ultra-
 44 thin pseudomorphic layer of W(110). This combination
 45 provides a template with a lattice parameter varying lat-
 46 erally over 10 % and with a controlled and rather inert W
 47 chemical interface, which may be used for the fast combi-
 48 natorial investigation of any growth or physical phenom-
 49 enon depending on strain. This may be performed
 50 with local probes such as electron, optical or scanning-
 51 probe microscopies, or with many nowadays synchrotrons
 52 offering beams focused to 100 μ m or smaller.

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- 16 A detailed discussion of RBS-channeling data will be addressed separately.