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Metallic Superlattices: The Study of Materials at Length Scales From a Few to Hundreds of Angstroms

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Abstract

We present the possibilities that metallic superlattices offer for the study of materials at length scales ranging from a few to hundreds of angstroms. The materials problems being studied span practically all interesting solid-state phenomena, including superconductivity, magnetism, elastic behavior, development of novel materials, diffusion, ion beam mixing, crystallization, and amorphization. Several applications are also being pursued. We present a few examples of problems that can be studied at different length scales. Emphasis is made that for a proper study of materials properties, extensive structural characterization is imperative.

Introduction

In recent years there has been a virtual explosion in studies related to the physics of layered and thin films.[1-3] Multilayers in which one of the elements is a metal have been used in basic studies of the nature of a large variety of physical phenomena.[1] The main reason for the versatility of multilayers is that layer thicknesses can be changed in order to study physical phenomena at length scales ranging from a few hundred angstroms (as for superconducting studies) to a few angstroms (as for two-dimensional magnetic studies). In addition, many potential applications are envisioned and some have already been implemented.

Although periodic metallic multilayers were first studied over 40 years ago,[4] the large increase in the work in this area has occurred only recently. Because the field is still developing, it is impossible to give a completely comprehensive, up-to-date review. We will use examples mostly from our own work to illustrate the type of physics that can be done at different length scales. Those interested in a more extensive and comprehensive review are referred to several recent books on the subject.[1,3]

Preparation and Characterization

Multilayered samples have been prepared by sputtering and by high- and ultrahigh-vacuum (UHV) thermal evaporation. UHV thermal evaporation, on heated substrates, is commonly designated as molecular beam epitaxy (MBE). To date, no detailed study has been directed toward understanding the difference in sample characteristics between the two preparation methods. In one case (Nb/Ta) in which films were prepared by both methods,[5,6] it has been claimed that the structures of the samples are similar.

The structural properties of importance for the multilayers are the composition profile in the direction perpendicular to the layers, the roughness, and the crystallinity. As a first structural tool, electron microscopy can be valuable in enabling one to observe the presence of the layered structure (especially for complex structures) and to make some statements regarding the substrate and interfacial roughness. For electron microscopy studies, a multilayered sample is cut in the form of a wedge, perpendicular to the layers (like a slice of birthday cake). Consequently, the electron beam is aimed parallel to the interfaces and a direct image of the layers can be obtained, as illustrated for a W/C Fabry-Perot structure in Figure 1.[7] The figure shows extremely well-formed layers at a superlattice periodicity of ~32.5 Å. An averaging phenomenon occurs along the electron path, however, and the roughness might appear to be less than in reality. To date, these techniques[7] have not been applied to all types of samples; in particular, metal/metal multilayers have not been extensively imaged this way. More sophisticated electron microscopy techniques, such as dark field imaging, have received even less attention as tools for studying the structure of multilayers.

To obtain information on the composition profile perpendicular to the layers, small angle x-ray and electron diffraction is useful. Figure 2 shows small angle x-ray diffraction data from a W (10.3 Å)/C (72.2 Å) multilayer prepared by sputtering. In principle, the peak intensities are just the Fourier transforms of the composition profile;[8] however, dynamic corrections complicate the interpretation. An alternative approach to understanding the small angle scattering relies on an intrinsically dynamic calculation, the Fresnel formalism. This approach, however, has weaknesses since it requires, for instance, *a priori* knowledge of optical constants of very thin films (generally assumed to be the same as in the bulk) and a scheme for introducing roughness, generally assumed to be Debye-Waller like.[9] Small angle scattering, therefore, is useful in determining layer thicknesses and in comparing the relative composition profiles of similar samples.

A multilayer structure with coherent stacking[10] of the atomic planes is commonly designated as a superlattice. The

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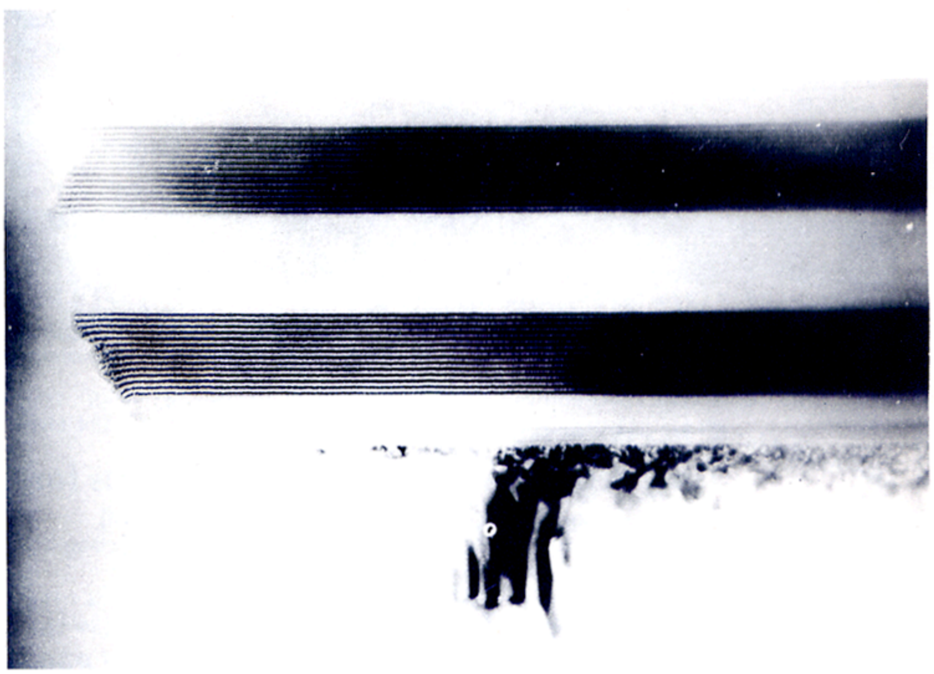

Figure 1. Transmission electron micrograph of a cross-section of a Fabry-Perot interferometer. The periodicity of the two C/W multilayers is 32.5 Å and the carbon spacer is 480 Å thick.

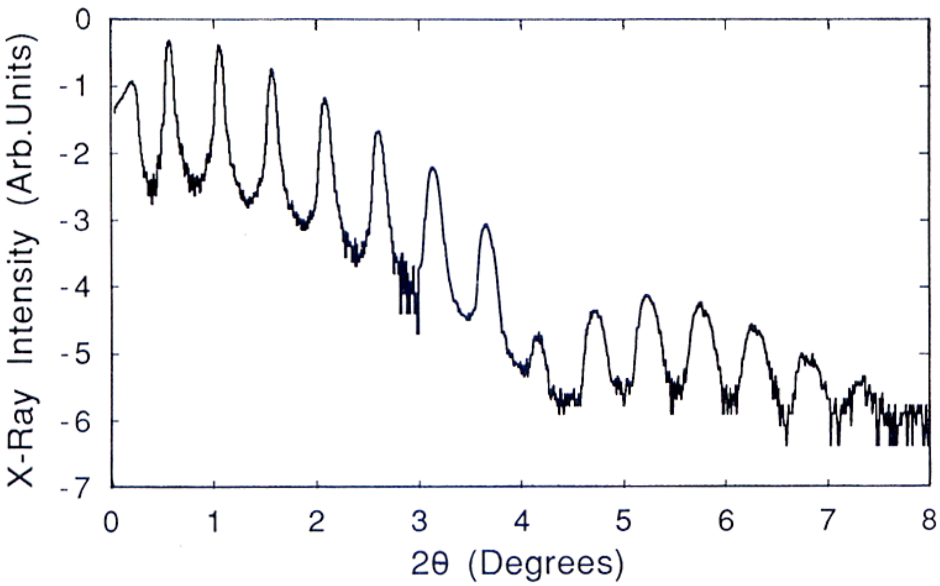

Figure 2. Small angle θ-2θ x-ray scan of an 8-bilayer W (10.3 Å)/C (72.2 Å) multilayer sample.

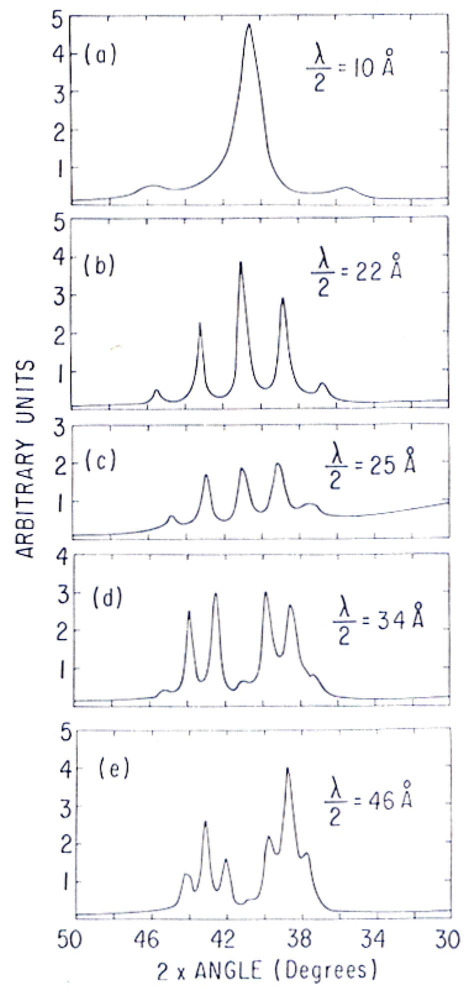

Figure 3. High angle θ-2θ x-ray scans of Cu/Nb superlattices with modulation periodicity λ of (a) 20 Å, (b) 44 Å, (c) 50 Å, (d) 68 Å , and (e) 92 Å.

high angle θ-2θ diffraction of a superlattice exhibits structure that is characteristic of this coherent stacking, as shown in Figure 3 for Nb/Cu superlattices. If the stacking is not coherent, the additional high angle "superlattice" peaks are absent. (High angle peaks can be obtained from finite size effects in the individual layers, even if coherent stacking is absent. These, however, have a different thickness dependence from the superlattice peaks.) Although many combinations can be grown as multilayers, only a few grow as superlattices, i.e., exhibiting high angle superlattice diffraction peaks. The reason for the growth of some combinations and not others in a superlattice is not understood at present. Although the nomenclature described above clearly distinguishes between multilayers and superlattices, the word "superlattice" has recently been adopted to describe any multilayer, coherently stacked or not.

To understand how well the crystalline axis of a superlattice is oriented in the z-direction, "rocking curves" are performed around the main perpendicular scattering direction. In the plane of the film, the structure can be polycrystalline or single crystal with various degrees of interfacial roughness. To determine the in-plane structure, diffraction experiments with the wavevector in the plane (Laue, in-plane θ-2θ, etc.) can be performed.

To obtain detailed structural information from high angle diffraction data, usually a model is constructed, the x-ray intensity calculated, and the model adjusted to fit the data by using adjustable parameters. In many cases, however, the number of possible parameters is much larger than the number of diffraction peaks, and therefore some error could be present in the precision with which the structure can be determined. Of course, if many different scattering measurements are performed (perhaps at different wavelengths) and the number of parameters is less than the number of experimentally measured peak intensities, the structure can be determined accurately.

Additional information about the surface structure can also be obtained by using *in situ* reflection high energy electron diffraction (RHEED) during growth. This type of measurement gives information on the crystalline structure and smoothness of the growing layer. The precision commonly obtained for interatomic spaces is typically 1%, and angular precision is about 5 degrees. Further theoretical and experimental work on the quantitative aspects of RHEED is necessary and should be pursued.

If the phenomenon to be studied occurs at long length scales (as in superconductivity), structural details at the monolayer level are not very important. However, if the physics of interest requires short length scales (as for magnetic exchange-coupling), details of the structure at the atomic level are crucial. We would like to stress that much interesting physics can be pursued at all length scales and therefore it is not always necessary to pursue ultimate perfection in the crystallinity, roughness, interdiffusion, etc. of the samples. Many tradeoffs are present; for instance, some samples exhibit a higher degree of crystallinity but are more interdiffused, and others exhibit very sharp interfaces but are polycrystalline.

Physical Properties

The ability to prepare layered materials at different length scales is useful for studying a number of interesting phenomena. A variety of causes for potentially interesting effects are present. These include changes in the structure due to epitaxial relations, changes in the electronic structure, the development of interfacial states, various proximity effects, electron transfer, variations of the thickness when compared to some characteristic length (for instance, dipolar length, superconducting coherence length, or exchange length), and so on. Depending on the length scale and/or physics under study, the structural characteristics of importance vary considerably. For instance, for the superconducting proximity effect, low interdiffusion is important, but crystallinity does not affect the results substantially. On the other hand, if long electronic mean-free paths are desired, crystalline perfection and coherent stacking are of major importance, but interdiffusion might be tolerated. Since the structural characteristics of importance vary depending on the length scale, it is

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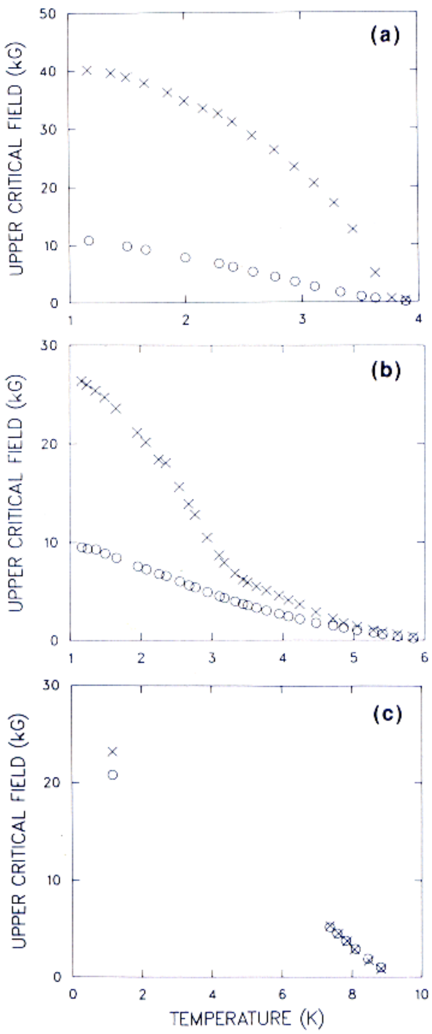

Figure 4. Parallel (crosses) and perpendicular (circles) upper critical fields, in three different regimes: (a) 2D, single film of Nb (191 Å); (b) crossover, 20-bilayer superlattice of Nb (172 Å)/Cu (333 Å) superlattice; and (c) 3D, single film of Nb (8500 Å).

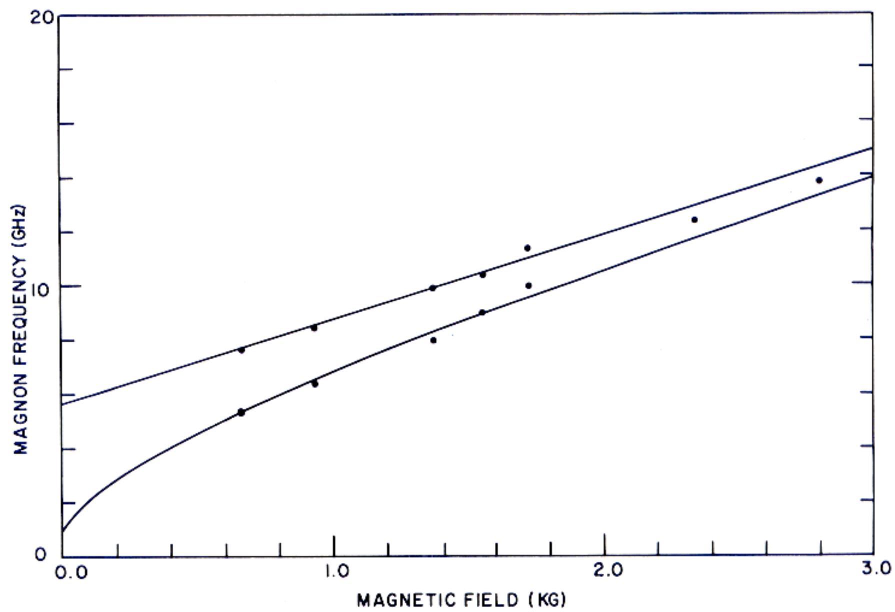

Figure 5. Field dependence of surface (lower curve) and collective mode (upper curve) magnons for Mo (83 Å)/Ni (249 Å) superlattice. Symbols are experimental data; curves are theoretical predictions.

convenient to arbitrarily divide the physical phenomena into two classes—long length scales (above 50 Å) and short ones (below 50 Å).

Long-Length-Scale Phenomena

The phenomena that occur at length scales larger than 50 Å include superconductivity, magnetic and electric dipolar coupling, interdiffusion, ion-beam-induced mixing, and solid-state amorphization.

Dimensional effects in artificial superconducting layers were observed for the first time by Ruggiero, Barbee, and Beasley[11] in the temperature dependence of the parallel critical fields, $H_{c2\|}$, of Nb/Ge multilayers. By preparing a stack of two-dimensional (2D) superconducting layers separated by semiconductors or normal metals, it is possible to observe the so-called "dimensional crossover" phenomena. If the nonsuperconducting separator is thick compared to the coherence length, the 2D layers are decoupled, and a typical square-root-like temperature dependence of $H_{c2\|}$ is observed (Figure 4a). On the other hand, if the separator is thin compared to the coherence length, the behavior is three-dimensional (3D), and the temperature dependence of $H_{c2\|}$ is linear (Figure 4c). Since the coherence length diverges close to the critical temperature T_c, it is possible to prepare samples that exhibit dimensional crossover as a function of temperature. Close to T_c, where the coherence length is long, the layers are strongly coupled and the behavior is 3D. At low temperatures, as the coherence length shrinks, the layers decouple and become 2D-like, with a square-root dependence of $H_{c2\|}$ (Figure 4b).

The first observation of collective effects in metallic superlattices was the development of magnon bands in Mo/Ni superlattices coupled by the magnetic dipolar interaction.[12] Owing to the dipolar coupling, in addition to the ordinary magnons in the individual Ni layers, a band of magnons develops. This band is similar to the electronic bands that develop when atoms are placed in a crystalline lattice. Figure 5 shows the magnetic field dependence of the magnon band and the surface magnon together with the corresponding theoretical predictions.[13]

It is clear that for these long-length-scale phenomena, small amounts of interfacial disorder or interdiffusion will not affect the results substantially. However, good thickness regularity across the whole stack might be important, as for the existence of magnon bands.

Short-Length-Scale Phenomena

The physical phenomena that can be envisioned at short length scales (below 50 Å) include observations of anomalous elastic constants,[14] RKKY and exchange coupling across normal metals, propagation of spiral magnetism across normal metals,[15] 2D magnetism,[16] localization effects in the transport properties,[17] stabilization of novel epitaxial phases,[18,19] and interfacially induced phenomena such as amorphization.[20]

Much of the initial impetus for research on metallic superlattices was provided by the observation of extremely anomalous elastic constant enhancements in lattice-matched Cu/Ni superlattices.[14] The origins of these enhancements are still not understood quantitatively. Later, our observations on nonlattice-matched Nb/Cu superlattices[21] showed a remarkable softening due to a lattice expansion in the structure. Figure 6 shows the observed phonon velocity as a function of interplanar atomic spacing, together with a no-adjustable-parameters molecular dynamics calculation. Although the lattice expansion satisfactorily explains the elastic constant anomaly, the origin of the expansion is not understood. Clearly, however, since the anomalous elastic properties occur for small layer thicknesses, an understanding of the structure at almost the atomic level is necessary.

RKKY coupling across a normal metal, Cu, in evaporated Cu/Ni superlattices was

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reported some time ago.[22] More recently, RKKY oscillations were observed in MBE-prepared Gd/Y superlattices.[23] The propagation of spiral magnetism across Y layers in Dy/Y superlattices[15] has been the focus of several structural and magnetic studies. A variety of novel phases have also been stabilized by epitaxially sandwiching one element within layers of another.[18]

Heteroepitaxial systems in sandwich and superlattice geometry can exhibit interesting phenomena.[24] New epitaxial orientations in fcc/bcc systems, and novel metastable phases induced by the interplay of geometrical and electronic properties, have been found in the MBE grown[25] Ce/V system. In the plane of the film, Ce films grown on V are contracted 8% (up to ~40 Å), but perpendicular to the film plane, the (111) atomic spacing is expanded less than 2% when compared to the bulk γ-Ce phase (see Figure 7). The origin of the new Ce phase is not well understood. However, the electronic structure of the 4f-electrons in Ce clearly plays an important role since purely epitaxial relations, together with Poisson's ratio, cannot properly explain the experimental observations.

Much theoretical effort has gone into understanding the details of the electronic structure of superlattices.[24] Many unusual phases and phenomena have been predicted in a variety of systems not yet available in the laboratory. In addition to these computer-intensive calculations, theoretical work is needed at the qualitative level to guide experimental studies and searches for novel phenomena.

Applications

Although metallic superlattices have received intense attention only in the last few years, various applications have been or are being developed. Resistor materials with low temperature coefficients of resistivity, high-coercivity multilayers, high superconducting critical field tapes, neutron optics,[26] and nonlinear optical elements are a few examples.

Perhaps the most important application to date has been in x-ray optics.[9] With the advent of high-intensity x-rays from synchrotrons and the development of the space telescope, there is an ever-increasing need for optics in the middle and soft x-ray wavelength, above ~5 Å. For this wavelength range, no adequate optical elements have been produced from naturally occurring materials. Metallic multilayers made from high-Z/low-Z combinations are ideal for this purpose; one notable example is the well studied W/C combination.[27] Mirrors of this type are currently in use in several places. However, considerable work is needed in two general areas—*materials development* (optimization of the constituents, improvement of the roughness, studies of radiation damage and thermal stability, etc.) and *optical elements development* (preparation of multilayers on complex shaped substrates, improved cooling methods, and so on).

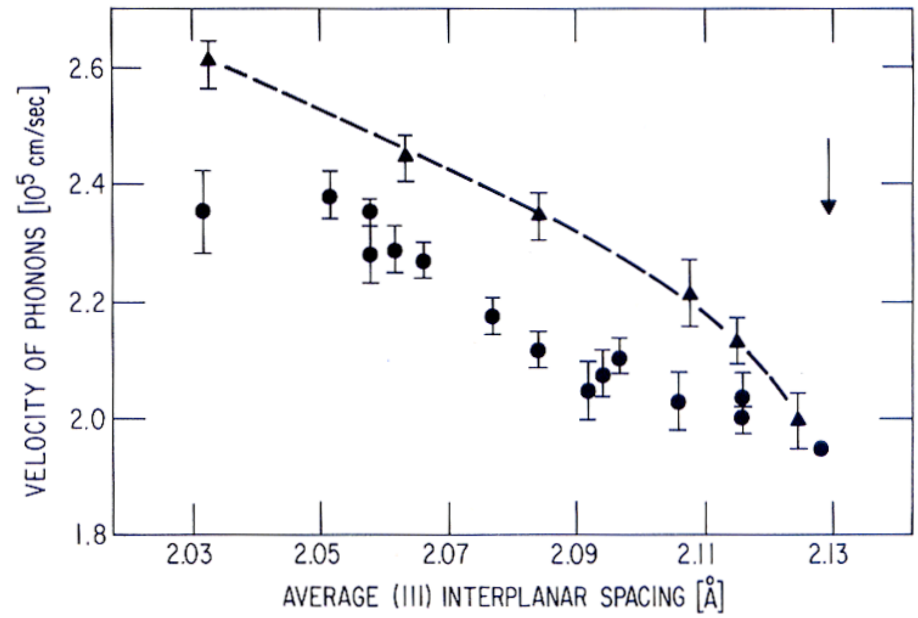

Figure 6. Softening of the shear modulus in Mo/Ni superlattices. Experimental plots of phonon velocity vs. interplanar spacing of Ni(111) from Brillouin and x-ray studies (circles) are compared with molecular dynamics simulations (triangles). The arrow indicates the unstable phase in the simulation which corresponds to order-disorder transitions in the superlattices.

Summary

Metallic multilayers have been a subject of investigation for many years. A renewed impetus in the past few years has come from the development of modern preparation techniques and from the discovery of intriguing and stimulating new physical phenomena. Metallic multilayers allow studies of condensed-matter phenomena on length scales from a few angstroms to hundreds of angstroms. Because of this wide range, a wealth of physical phenomena can be studied, and the problems amenable to investigation are limited only by imagination. Perhaps this is a good opportunity to ask the reader to join this exciting field if she/he has not already done so.

Acknowledgments

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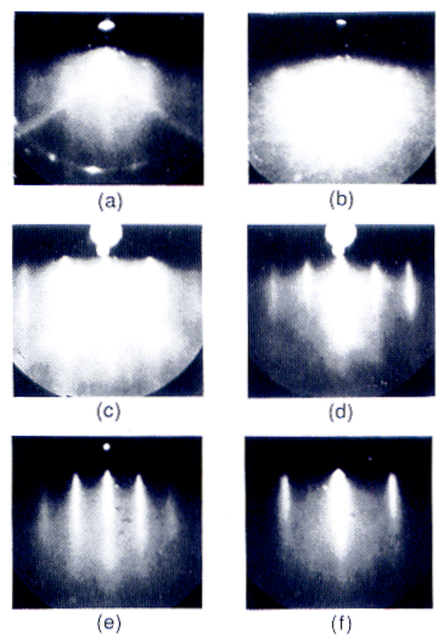

Figure 7. 10-keV RHEED patterns of the epitaxial Ce/V system. (a) and (b): sapphire substrate ($11\bar{2}0$) of azimuths [0001]α-Al_2O_3 and nearly [$\bar{1}104$]α-Al_2O_3. (c) and (d): 1000 Å V(110) of $[\bar{1}1\bar{1}]_v$ and $[\bar{1}10]_v$. (e) and (f): 50 Å Ce(111) of $[\bar{1}12]_{Ce}$ and $[1\bar{1}0]_{Ce}$. The absolute angles are 30° in (a) and (c), 65° in (b) and (d), 94° in (e), and 3° in (f).

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