

Chemistry for the 21st Century

Interfacial Science

Edited by M.W. Roberts

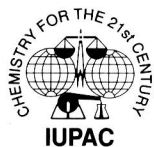
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Interfacial Science

A 'Chemistry for the 21st Century' monograph

EDITED BY

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Foreword



The instigation of the series of books of which this one forms an integral part, owes a great deal to Kirill Ilyich Zamaraev, former President of the International Union of Pure and Applied Chemistry (1993–95). News of his death in June 1996 caused grief in many corners of the world. But the memory of his gifts and talents lives on, not least in books such as these — there were many others — that were stimulated by his concerns, enthusiasms and perspicacity.

Many tributes have already been paid to the life and work of Kirill Zamaraev (see, for example, *Mendeleev Communications*, 1996, 213 and *Catalysis Letters*, 1996, Vol. 41, No. 1,2, p(i)). Doubtless many more will be composed. What needs to be emphasised about Kirill Zamaraev, however, is that he combined in a remarkable way the ability to be forward-looking, with a deep awareness and appreciation of the past. Whilst he loved the past, he did not live in it. But the finest tradition bequeathed to us by great human beings was something of which he was acutely and sensitively aware. Even while lying ill in a Moscow hospital in the autumn of 1994 he wrote a beautiful booklet that chronicles the achievements of Russian scientists in catalysis from the days of Lomonosov (1711–65) onwards.

To some thinkers, tradition is, by definition, an irrational inheritance from the dead past, a mere residue of obsolete beliefs and customs which an enlightened society, especially scientists, should discard as an impediment to reason and progress. Kirill rejected such arguments: we owe as much to the traditions of our scientific predecessors as we do to their discoveries and inventions. This ethos always shone through whenever one had a philosophical talk with Kirill. I shall always treasure his quotation from Pushkin: ‘How many and varied are the discoveries prepared for us by the spirit of the

enlightenment, by experiment, the child of error and effort, by genius, the friend of paradox, and by that divine inventor, chance'.

He would be proud of this book.

Sir John Meurig Thomas
*Royal Institution of Great Britain, London,
and Peterhouse, University of Cambridge*

Preface

It was Kirill Zamaraev who, on a visit to Cardiff to deliver the Royal Society of Chemistry Centenary Lecture in 1995, invited me to edit this monograph on Interfacial Science. I had first met Professor Zamaraev at the Indian National Science Academy's Golden Jubilee Symposium held in New Delhi in 1984. This led to a most fruitful collaboration with two of his colleagues at the Institute of Catalysis in Novosibirsk, A. Boronin and V. Bukhtiyarov. We agreed that the monograph should not dwell exclusively on surface science, heterogeneous catalysis or materials science; rather that it should reflect the wider perspective of interfacial science. It was, therefore, with this very much in mind that I approached the authors of these eleven articles.

The ability to design a solid surface with specific properties, whether as an efficient and selective catalyst or for the creation of a new optical device, has been a central theme in both fundamental and applied research over the last two decades. It has not only been driven by technological demands but also through academic curiosity and the emergence of sophisticated surface-sensitive techniques which have provided precise answers to previously unanswerable questions. In addition, and especially over the last decade, computational methods have been developed which have played an important role in constructing models of surfaces and the associated chemistry of a wide range of solid materials; these methods have already opened up new avenues for application and for fundamental thinking. The largely unpredictable nature of molecular events at surfaces does, however, emphasise the need to ensure that the computational results need always to be assessed against the relevant experimental data.

In this monograph we see a blurring of the traditional approaches to condensed phase and surface chemistry:

- surface modelling as a development of bulk computational methods (Catlow *et al.*);
- whether oxygen states present at metal surfaces mimic those at bulk oxide surfaces (Carley and Davies; Onishi and Iwasawa);
- the chemistry and model of growth of small metal clusters compared with the characteristics of the corresponding bulk metal surfaces (Bukhtiyarov; Tomellini and Fanfoni);
- growing single-crystal films of complex metal oxides by epitaxial or vapour deposition methods (Rao *et al.*; Williams *et al.*);
- studying semiconductor surfaces at 'high' pressures using new experimental techniques (Pemble);
- controlling the properties of polymer surfaces by plasma etching (Wheale and Badyal);
- the technological implications of novel inclusion compounds (Harris); and
- the role of hot electrons in surface reactions (Otto *et al.*).

The authors provide both authoritative and critical accounts of the present status of their research topics which will appeal to a wide spectrum of surface scientists.

M.W. Roberts

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Solid–Solid Interfaces in the Epitaxial Films of Complex Oxides Deposited by Chemical Methods

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1 Introduction

The term *epitaxy* literally means ‘arrangement upon’; it describes the oriented growth of one crystalline material (guest) on the surface of a single crystal of a different material (substrate). The adjective *epitaxial* implies not only that one particular crystal plane of the deposited guest crystal (deposited film) comes into contact with the surface of the host crystal, but also that one particular crystallographic direction in the contact plane of the guest crystal is parallel to a specific crystallographic direction in the contact plane of the host crystal. This is usually described in terms of Miller indices of the crystal planes and directions. For instance, (001)F [100]F// (001)S [100]S means that the (001) plane of the deposited film is in contact or aligned with the (001) plane of the substrate surface and that the [100] film growth direction coincides with the [100] direction of the substrate surface. For epitaxial growth to occur, it is desirable to have good lattice matching between the material of the film and the substrate, which would alleviate the problems of stress and relaxation through the formation of misfit dislocations. Another requirement for epitaxial nucleation is that the surface energy of the nucleus–substrate interface should be lower for the epitaxial orientation than for other orientations, so that the nucleation rate for the epitaxial orientation is greater. However, epitaxy can also occur due to different growth processes.

Preparation of single-crystalline films of complex oxides by means of epitaxial growth on suitable single-crystal substrates is an important area of research today because of the extensive, sophisticated technological applications of the epitaxial films in various types of devices. The single-crystalline or epitaxial nature of a film is established by X-ray diffraction techniques and more particularly by direct observation of the interface between the substrate and the deposited film by means of high-resolution transmission electron microscopy (HRTEM). By studying HRTEM images, one can determine how good the lattice match is between the lattice of the deposited film and that of the substrate. One can estimate the strain at the interface based on the mismatch, besides observing structural defects at the interface. In recent years, excellent single-crystalline (epitaxial) films of ferroelectric oxides such as PbTiO_3 and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and other complex oxide systems have been prepared on different single-crystal substrates by several techniques [1–8]. A few important deposition techniques are: (i) pulsed laser deposition (PLD); (ii) molecular beam epitaxy (MBE); and (iii) metal–organic chemical vapour deposition (MOCVD). Of these three methods, MOCVD is truly a chemical method involving reactions of

precursors, while PLD involves the physical process of transferring the material from the target to the substrate. MBE involves vaporisation and monolayer deposition, followed by chemical reaction of the layers at the atomic scale. All three methods have yielded high-quality films, but they are all expensive and need sophisticated instrumentation. This is especially true of MBE.

In our laboratory, we have established inexpensive but powerful techniques for preparing oriented films of complex oxides by nebulised spray pyrolysis. In this paper, we shall briefly describe the PLD, MBE and MOCVD methods and illustrate results obtained by them with respect to epitaxial films of complex oxides on single-crystal substrates. The single-crystal substrates are generally oxides such as MgO, SrTiO₃ (STO) and LaAlO₃ (LAO), giving rise to oxide–oxide (solid–solid) interfaces. We provide a detailed description of the results on thin films of complex oxides obtained by nebulised spray pyrolysis and demonstrate how this inexpensive technique gives excellent-quality epitaxial films of complex oxides of technological importance, which include ferroelectric PbZr_xTi_{1-x}O₃ ($x = 0.5$), metallic LaNiO₃, and LaMnO₃ which exhibits giant magnetoresistance (GMR). In so doing, we describe the method in some detail and provide the HRTEM evidence for the epitaxial nature of the films obtained by this technique, showing the presence of an excellent lattice match between the deposited film and the substrate.

2 Pulsed laser deposition

In PLD, the material is evaporated from a target composed of the stoichiometric solid by means of an intense pulsed laser beam [9–12]. An excimer laser (KrF type, with a wavelength of 248 nm and a pulsewidth of *c.* 30 ns, operated at 100–1000 mJ pulse energy and a typical repetition rate of 1–10 Hz) is generally employed. A lower-power HeNe laser is employed to align and focus the excimer laser on to the target. The PLD process can be classified into three regions.

- 1 Absorption of the laser radiation by the target material resulting in the ablation (evaporation) of the surface layer.
- 2 Interaction of the evaporated material with the laser beam during which the evaporated ions and atoms absorb the photon energy.
- 3 Anisotropic adiabatic expansion of the plasma resulting in a forward-directed plume.

The epitaxial growth of the oxide superconductors on single-crystal substrates is required for microwave and other applications. LAO is a strong candidate as a substrate for superconducting thin films for microwave applications due to its low dielectric constant and loss tangent [13]. Although the actual structure of LaAlO₃ at room temperature is rhombohedral, its unit cell can be described as a slightly distorted pseudocubic perovskite providing a close lattice match with the unit cell of YBCO. Highly epitaxial thin films of YBCO have been obtained on (001) single-crystal LAO by PLD [14]. An HRTEM image of the interface between the YBCO film and the LAO substrate is presented in Fig. 1.1. The image shows near-perfect epitaxial *c* perpendicular growth of YBCO on (001) LAO. This interface microstructure also reveals the presence of regions of strain which extend into both the film and the substrate. These strained regions correspond to interfacial dislocations. The presence of interfacial dislocations is due to the slight mismatch of the lattice parameters of YBCO and LAO.



Figure 1.1. HRTEM image of the interface between the YBCO film deposited by PLD and the LaAlO₃(001) substrate. The inset SAED pattern taken from an area including both the film and the substrate confirms the epitaxial growth. The presence of an interfacial dislocation is seen in form of an extra half-plane in the substrate within the marked regions. From [14].

The epitaxial *c* perpendicular growth of the YBCO film is further confirmed by the selected area electron diffraction (SAED) pattern which is taken from an area at the interface including both the film and the substrate (see inset Fig. 1.1). The coincidence of the diffraction spots of the film and the substrate shows the epitaxial nature of the film. The epitaxial relationship is (001)YBa₂Cu₃O_{7-x}//(001)LaAlO₃. Another example of an epitaxial film obtained by PLD is illustrated in Fig. 1.2 [15]. The figure shows an HRTEM image of a PbTiO₃ film on an (001)STO substrate. This image reveals a perfect in-plane matching and a complete absence of *a*-axis-oriented domains establishing the *c*-axis orientation of the film. The SAED pattern shown in the inset also confirms the *c*-axis orientation of the film. The orientation relationship of the film and the substrate is (001)PbTiO₃//(001)SrTiO₃.

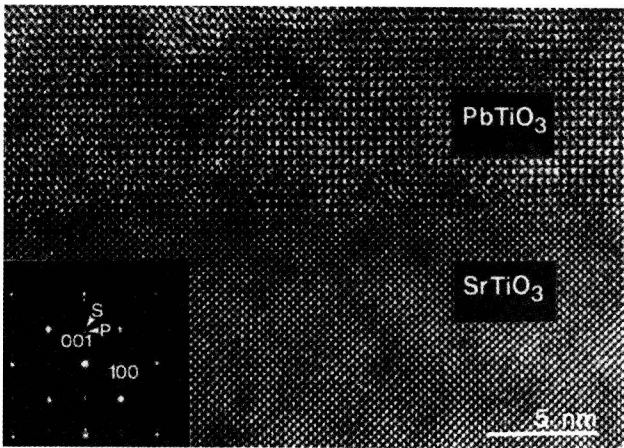


Figure 1.2. HRTEM image of the interface between a PbTiO₃(P) film deposited on the SrTiO₃(001) substrate by PLD showing perfect in-plane matching. The SAED pattern shown in the inset also evidences the *c* orientation of the PbTiO₃ film. From [15].

3 Molecular beam epitaxy

MBE is a versatile technique for growing epitaxial films of metals, semiconductors, insulators and oxide materials [16,17]. In this technique, molecular beams of the constituent atoms formed from Knudsen effusion cells are allowed to impinge on a heated substrate under ultra-high vacuum (*c.* 10^{-10} torr). The heated substrate provides the impinging molecules with sufficient energy to be mobile on the substrate so that these atoms migrate on the surface until they encounter an appropriate site on which to condense. Under satisfactory conditions, one obtains the growth of a single-crystal epitaxial film on a single-crystal substrate. Typical rates used for deposition in MBE are about one atomic layer per second. The rate of deposition is controlled by the intensity of the molecular beam. Therefore, the uniformity of the film depends on the uniformity of the beams. Thus, the MBE process offers a high degree of uniformity, controllability and reproducibility. In the MBE system, several beams of different substances can be operated in the same chamber and directed on to the substrate surface. Given the independent control of the intensities of the beams and the control of the substrate temperature, structures of the prescribed composition with a variety of layers can be deposited in the form of a film. MBE has been used to prepare high-quality epitaxial films of a variety of oxides as well as superlattices on different single-crystal substrates. One of the important applications of the ferroelectric perovskite BaTiO_3 is in electro-optic devices. The large electro-optic coefficient of BaTiO_3 , coupled with the small microwave dielectric constant of a substrate such as MgO , could substantially improve the device speed and efficiency. Devices based on these materials in thin-film form require long-range structural coherence at the interface, which can be realised in epitaxial thin films. Epitaxial BaTiO_3 films have been prepared on a MgO substrate by using MBE [18]. Figure 1.3 shows a scanning electron micrograph of BaTiO_3 on $\text{MgO}(001)$ in cross-sectional view. We see that the film is $0.6\text{ }\mu\text{m}$ thick, crack-free, dense, single-phase and optically transparent. Figure 1.4 shows an HRTEM image of the BaTiO_3 – MgO interface. The cube-on-cube epitaxy can be readily observed in this image. At a larger scale, the HRTEM images showed dislocations nucleated to relieve the interfacial strain.

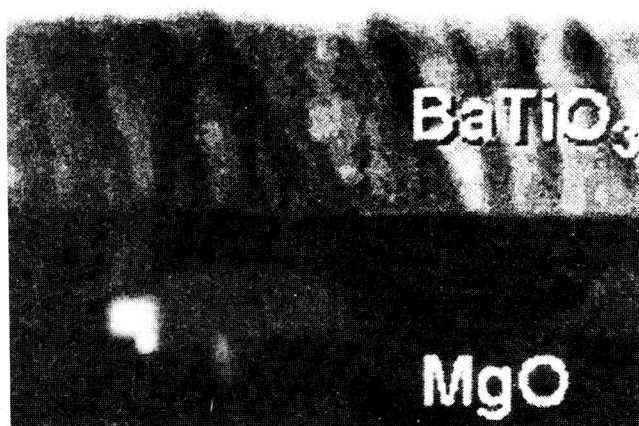


Figure 1.3. Cross-sectional scanning electron micrograph of BaTiO_3 film deposited on $\text{MgO}(001)$ by MBE. Film thickness is $0.6\text{ }\mu\text{m}$. From [18].

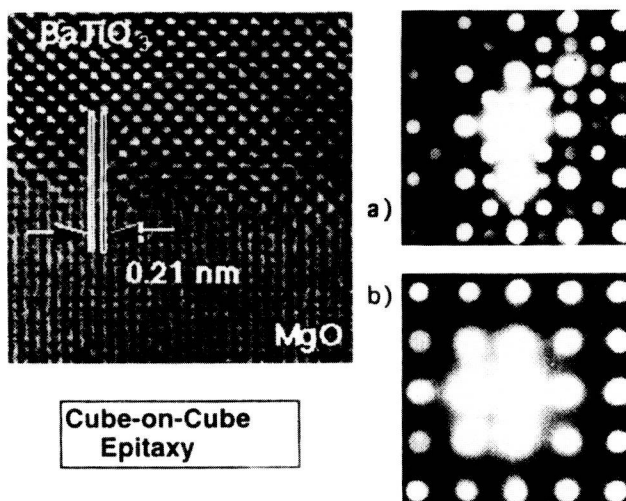


Figure 1.4. HRTEM image of the BaTiO₃-MgO(001) interface (in a film obtained by MBE) with the SAED pattern inserts from: (a) BaTiO₃; (b) MgO. From [18].

4 Metal-organic chemical vapour deposition

In MOCVD, a metal-organic precursor compound or combination of precursor compounds from the gas phase condenses on a substrate surface where a chemical reaction occurs, leading to the formation of a solid film [19]. If the (source) material to be deposited is not in the vapour state, it can be converted into the vapour state by volatilising from either the solid or the liquid source. In its most common form, the CVD process relies upon elevated substrate temperatures to pyrolyse the gaseous precursor for film growth. However, when high growth temperatures are incompatible with the substrate material, or when metastable materials are to be deposited, it is necessary to activate the chemical reaction near or on the surface to facilitate film growth at reduced temperatures. This is accomplished by the application of a radio-frequency (RF) field (plasma excitation), light (photoexcitation) or by direct heating of the gaseous source (thermal excitation). MOCVD has been widely employed for the deposition of epitaxial ferroelectric films. An epitaxial ferroelectric BaTiO₃ film is obtained on a MgO(100) substrate by MOCVD at 875 K by using titanium isopropoxide and bis(2,2,6,6-tetramethyl 3,5 heptanedionato)barium, i.e. Ba(thd)₂, as precursors [20]. An HRTEM image of this BaTiO₃ film, showing the BaTiO₃-MgO interface, is shown in Fig. 1.5(a). We see that the (200) lattice planes are continuous across the interface, demonstrating the epitaxial nature of the film. The image also shows that the film-substrate interface is sharp and contains no second phases. Misfit dislocations in the BaTiO₃ film were observed at the interface. One such dislocation is indicated by an arrow in the micrograph. Formation of the dislocations probably occurred during the deposition process in order to accommodate the 5.4% lattice mismatch between the substrate and the growing film at the growth temperature. The SAED pattern of the BaTiO₃-MgO interface shown in Fig. 1.5(b) shows a cube-on-cube orientation between BaTiO₃ and MgO (i.e. alignment of both normal and in-plane lattice vectors of the film with that of the substrate) confirming that the film is epitaxial. Higher-order diffraction spots showed some arcing, indicating that the different regions of the film were slightly