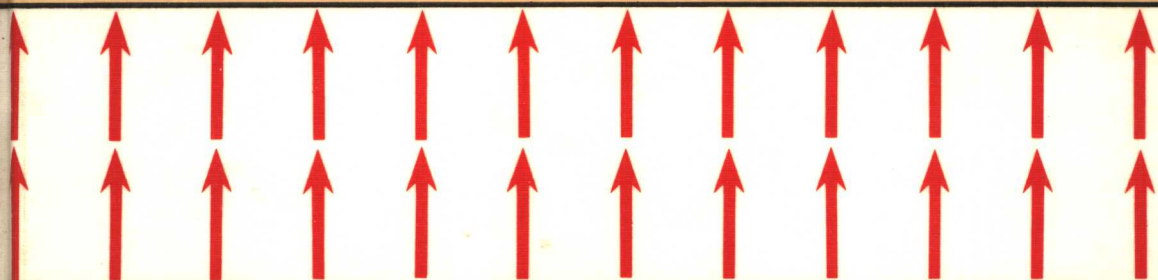


Handbook of Magnetic Materials

Edited by
K. H. J. Buschow

VOLUME

7



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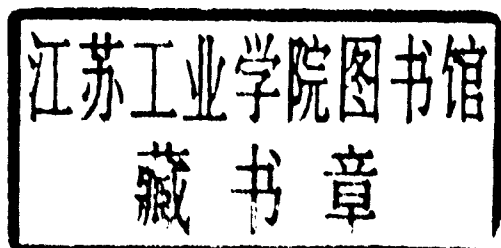
HANDBOOK of MAGNETIC MATERIALS

VOLUME 7

EDITED BY

K.H.J. BUSCHOW

Philips Research Laboratories
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PREFACE TO VOLUME 7

The original aim of Peter Wohlfarth when he started this Handbook series was to combine new development in magnetism with the achievements of earlier compilations of monographs, to produce a worthy successor to Bozorth's classical and monumental book **Ferromagnetism**. It is mainly for this reason that **Ferromagnetic Materials** was initially chosen as title for the Handbook series, although the latter aims at giving a more complete cross-section of magnetism than Bozorth's book.

During the last few years magnetism has even more expanded into a variety of different areas of research, comprising the magnetism of several classes of novel materials which share with ferromagnetic materials only the presence of magnetic moments. This is the reason why the Editor and the Publisher of this Handbook series have carefully reconsidered the title of the Handbook series and have come to the conclusion that the more general title **Magnetic Materials** is more appropriate than **Ferromagnetic Materials**. This change in title has become effective starting with Volume 6. It is with great pleasure that I can introduce to you now Volume 7 of this series.

A substantial step forward in the understanding of metallic magnetism has been reached by means of electronic band structure calculation. Progress in this area has been made not only due to the availability of high speed computing machines but also due to sophistication in the computational methodology. In Volume 7 two chapters are devoted to this subject, one chapter dealing primarily with the elements and one chapter dealing primarily with 4f and 5f systems, including examples of the large group of intermetallic compounds. In both chapters the authors have concentrated on explaining the physics behind these band calculations. Their chapters are written in a manner understandable also to those scientists having no experience with band calculations.

Thin film technology has become a key issue in high density magnetic and magneto-optical recording. Both topics will be dealt with in future volumes of this Handbook series. As a precursor and as a sound basis for these topics the present volume contains a chapter on the magnetism of ultrathin transition metal films, describing the richness in novel magnetic phenomena that has been encountered in the past few years in these materials.

Of equal interest are the novel magnetic phenomena observed when magnetic

moments are incorporated in a semiconducting matrix. A comprehensive description of these materials is found in the chapter on Diluted Magnetic Semiconductors.

A separate chapter is devoted to the progress made in the field of heavy fermions and valence fluctuations, the emphasis being on the important results obtained by means of neutron scattering.

The magnetic properties of various types of rare earth based intermetallic compounds were reviewed already in Volume 1 of this Handbook series. However, the compounds in which rare earth elements are combined with 3d transition metals have received renewed interest in the last decade, which is due in part to the success of novel permanent magnet materials. Proliferation of scientific results obtained with novel techniques, and made for a large part on single crystals, have led to a more complete understanding of the basic interaction in these materials. A comprehensive description of the progress made in this field since the appearance of Volume 1 is given in the chapter on Magnetic Properties of Binary Rare-Earth 3d-Transition-Metal Inter-metallic Compounds.

Volume 7 of the Handbook on the Properties of Magnetic Materials, as the preceding volumes, has a dual purpose. As a textbook it is intended to be of assistance to those who wish to be introduced to a given topic in the field of magnetism without the need to read the vast amount of literature published. As a work of reference it is intended for scientists active in magnetism research. To this dual purpose, Volume 7 of the Handbook is composed of topical review articles written by leading authorities. In each of these articles an extensive description is given in graphical as well as in tabular form, much emphasis being placed on the discussion of the experimental material in the framework of physics, chemistry and materials science.

The task to provide the readership with novel trends and achievements in magnetism would have been extremely difficult without the professionalism of the North-Holland Physics Division of Elsevier Science Publishers and I would like to thank Anita de Waard and Fer Mesman for their great help and expertise.

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chapter 1

MAGNETISM IN ULTRATHIN TRANSITION METAL FILMS

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1. Introduction

In discussing magnetic thin metal films, we may distinguish intrinsic from defect-induced magnetic thin film phenomena. The first group includes phenomena which are connected with the finite thickness ('size effects' like the dependence of the Curie temperature and spontaneous magnetization on film thickness) and the existence of two surfaces ('surface' effects like magnetic surface anisotropies or modified magnetic moments in surfaces or interfaces). In addition, because films can be prepared only on substrates, the interaction with these substrates and their magnetic implications must be considered as intrinsic film phenomena. On the other hand, thin films are usually prepared by condensation from a highly supersaturated atomic beam and therefore contain a high level of defects. Depending on the vacuum level used in the preparation, a high level of impurities must be considered, too. A rich variety of interesting magnetic properties is connected with the resulting defect- and impurity-structure of thin magnetic films, in particular polycrystalline ones. They depend in a complicated manner on the preparation conditions, as discussed in the reviews of Jaggi, Methfessel and Sommerhalder (1962) and of Wijn (1988). The opportunities which are given by this broad spectrum of defect-induced magnetic thin film phenomena are widely used in magnetic thin film applications.

Because of their connexion with basic theoretical models, intrinsic magnetic film phenomena are of considerable interest for the understanding of fundamental magnetic phenomena, like magnetic order in lower dimensions. They have been discussed for a long time in this context only. However, following the success of molecular beam epitaxy (MBE) for semiconductors, the application of high-quality epitaxial magnetic thin films, and multilayers consisting of them, have been realized during the last years. MBE-grown magnetic multilayers are now candidates for high-density information storage. With increasing structural quality of these systems, intrinsic thin film properties become more and more important for applications, also.

The aim of the present review is a report on intrinsic magnetic thin film phenomena in epitaxial films of 3d-metals, the main concern being given by magnetic single films. Magnetic coupling phenomena in sandwiches and multilayers became recently a rapidly developing field, which deserves a separate review; we restrict ourselves to a short sketch of this timely subject, the full discussion of which is out of the scope of the review. In addition, magnetic multilayers will be reported, somewhere, as systems in which magnetic single film phenomena can be observed conveniently because of multiplication of the volume. In agreement with the general philosophy of this hand-

book, the review presents an experimental approach. Basic ideas of theoretical models will also be reported, however. In stressing intrinsic film phenomena, we are aware of the fact that the influence of the real and defect structure on the magnetic properties remains considerable even in the most sophisticated epitaxial films. Methods of epitaxial film preparation and structural testing will, therefore, be included. Being restricted to magnetic films which are dominated by intrinsic magnetic film phenomena, the report definitely excludes the extended body of application-oriented magnetic thin film research, in particular on polycrystalline films. Further, films containing rare earths are outside the scope of the review; they will be discussed in other contributions of the present volume.

Essential aspects of the subject are covered by several volumes of collected articles (Falicov and Moran-Lopez 1986, Falicov et al. 1990, Farrow et al. 1987, Jonker et al. 1989), and by special issues of *Applied Physics* edited by Pescia (1989). For a systematic collection of very thin epitaxial magnetic thin film data compare Gradmann (1988). For previous coherent presentations of the field see Gradmann (1974) and Gradmann et al. (1985).

The organization of the present review is based on the fact that any meaningful experimental research on intrinsic magnetic film properties depends on the preparation and structural testing of appropriate samples, and on experimental probes for magnetic order in films with monolayer sensitivity. After the present introduction, we therefore report on these preconditions of magnetic thin film analysis in the first main part consisting of sections 2–4 on guidelines of metal epitaxy, methods of structural analysis and probes of magnetic order, respectively. Magnetic thin film phenomena are then reported in the second main part in sections 5–9.

PART I. Preconditions of magnetic thin film analysis

2. Guidelines of metal epitaxy

Ultrathin magnetic metal films usually are prepared, using MBE or sputtering techniques, with growth rates which are many orders of magnitude larger than the rates of re-evaporation. Accordingly, growth proceeds in a quenching mode with high supersaturation, far from equilibrium, even at elevated temperatures of the epitaxial substrate, and is therefore far from being understood in detail. The resulting film structures therefore always have to be tested by the methods to be discussed in the next chapter. Extended reviews on epitaxial growth have been written by Matthews (1975a), Bauer and van der Merwe (1986) and Markov and Stoyanov (1987). We restrict our present discussion to some basic models and principles, which, though simplifying some aspects of a complicated subject, turned out to be useful in predicting and understanding epitaxial growth modes and film structures.

2.1. Surface energies and equilibrium growth modes

Bauer (1958) was the first to note that growth modes of thin films can be considered as a wetting problem, governed by $\Delta\gamma = \gamma_f + \gamma_i - \gamma_s$, where γ_s , γ_f and γ_i are the surface

energies of substrate and the growing film and the interface energy, respectively. If the film grows near equilibrium, it wets the surface and therefore starts growing by a monolayer if $\Delta\gamma < 0$; it starts growing by three-dimensional nuclei when $\Delta\gamma > 0$ (*Volmer-Weber mode of growth, island mode*). For the case of a stable monolayer, a further layer-by-layer growth (*van der Merwe mode, layer-by-layer mode*) is expected only if each layer wets the previous one, otherwise 3D nuclei are expected on one or a few flat layers (*Stranski-Krastanov mode*). Because of strain energies, which must be included in the surface energies of layer-grown film, whereas they can relax in 3D nuclei, plane van der Merwe mode is extremely rare. Because metallic interface energies are one order of magnitude lower than surface energies, the growth mode is governed essentially by surface energies. They are hard to measure. Some data for the magnetic 3d-metals Ni, Co and Fe are reported in table 1, in comparison with frequently used substrate metals. Considering all restrictions given by the application of these equilibrium considerations to the supersaturated growth, by the temperature dependence, anisotropy and overall uncertainty of surface energies, and by the application of the surface energy concept to monolayers, the data reduce to a rough rule that monolayer nucleation of Ni, Co and Fe can be expected on the high melting, high surface-energy substrates Mo, Re, Ta and W, but not on Cu, Ag and Au. It will be shown below that this rule fits to the available experience. Because A does not wet B if B wets A, flat multilayers cannot be grown near equilibrium.

TABLE 1

Free surface energies of metals and heats of adsorption for metals on metals. Experimental values γ (in mJ/m^2) for free surface energies of metals, from Mezey and Giber (1982), at lowest available temperatures; ground state values γ^0 from Miedema and Dorleijn (1980) for comparison. Heats of adsorption ΔH_{AB} for adsorption of adsorbate metal A on substrate metal B (in kJ/mol) from Miedema and Dorleijn (1980).

	Adsorbate A											
	Ag	Au	Mn	Cu	Pd	Ni	Co	Fe	Pt	Mo	Ta	W
γ (mJ m^{-2})	1.25	1.55	1.6	1.85	2.1	2.45	2.55	2.55	2.55	2.95	3.05	3.3
γ^0 (mJ m^{-2})	1.1	1.4		1.7		1.8	2.0	2.0		2.0	2.7	2.9
Substrate B	ΔH_{AB} (kJ mol^{-1})											
Ag	225	275	185	230	230	250		200				
Au	255	295	235	260	245	280		250				
Mn	265	315	220	245	285	300		260				
Cu	265	325	230	265	280	295		250				
Pd	295	335	285	295	285	320		300				
Ni	285	345	285	295	305	340		315				
Co	285	355	285	295	315	345		320				
Fe	275	355	280	285	320	345		315				
Pt	320	360	320	320	310	355		340				
Mo	295	395	295	305	365	380		345				
Ta	345	460	315	335	430	415		305				
W	310	405	315	315	375	390		360				

An alternative approach to the growth modes is given by heats of adsorption of metals on metals, as determined from thermodynamic data and tabulated by Miedema and Dorleijn (1980). Monolayer nucleation of A on B is then expected if the magnitude of the heat for adsorption of A on B, $\Delta H_{A,B}$, is larger than $\Delta H_{A,A}$. We include in table 1 values of $\Delta H_{A,B}$; both criteria, from ΔH and from $\Delta\gamma$, agree in their main message on growth modes.

2.2. Supersaturation and forced layer growth

Because of the high supersaturation of the condensing atomic beam, the real growth process is determined to a large extent by kinetic principles. It is then a general experience, both for epitaxial and polycrystalline films, that condensation at low temperatures results in small grain sizes, at high temperatures in large grains. The cause for this is that the atomic beam condenses, for the case of high supersaturation (low temperatures, high growth rates), by many small critical nuclei. Markov and Kaischew (1976) showed how size and volume of critical nuclei in epitaxial films depend on surface energies and supersaturation and that effective monolayer nucleation can be expected as soon as the height of the critical nucleus becomes as low as the distance of atomic layers. Accordingly, monolayer nucleation can be induced by high supersaturation, which means either low substrate temperatures or high evaporation rates, resulting in what is called a *quasi van der Merwe or forced layer growth mode*. A quantitative confirmation of the theory was performed by Gradmann and Tillmanns (1977), who observed for γ -Fe films on Cu(111) a transition from island growth, as expected from wetting considerations (compare table 1), to layer growth, which could be induced either by high evaporation rates or reduced growth temperatures. It is this supersaturation-induced, forced layer growth which enables more or less layer-grown epitaxial films even in nonwetting systems near the wetting limit, and therefore enables the growth of metallic superlattices if the surface energies of the components are similar. The situation is qualitatively different in semiconductor superlattices, where the different components are frequently given by lattice-matched, nearly equal crystals, which differ only by having a different doping to change their electrical properties and show nearly identical surface and negligible interface energies, resulting in the well-known possibility of growing superlattices with a quality which may be hard to achieve in metallic systems. In turn, layer growth of metal epitaxial films turns out to be mostly a delicate balance between forcing layer growth by supersaturation, which requires low temperatures, and good crystalline order, which requires high ones. We should note at this point that the notion of epitaxy, as introduced by Royer (1928), means only oriented growth of some crystal on an epitaxial substrate, be it of the same material (*autoepitaxy*) or another one (*heteroepitaxy*), independent of growth mode and lattice matching. An epitaxial film can, according to this definition, consist of few large, defect-free crystallites in parallel orientation, which grow together to a continuous film only in a later state of growth ('coalescence'), e.g. epitaxial metal films on NaCl, molybdenite or mica. For a review compare Pashley (1956, 1965) and Matthews (1975). Optimum epitaxy of defect-free crystals and layer growth are competing, for metal films.

2.3. Misfit and misfit dislocations

A second important parameter determining epitaxial growth is the *lattice misfit*, f , defined in a one-dimensional model by

$$f = (b - a)/a, \quad (2.1)$$

where b and a are the lattice parameters of film and substrate, respectively. This definition applies too for interfaces, if the contacting lattice planes of both crystals show the same two-dimensional symmetry (homosymmetric interfaces). Besides parallel orientated crystals with common 3D-symmetry, homosymmetric epitaxial systems include systems like hcp (0001) on fcc (111), with densely packed hexagonal planes in contact, and bcc (100) on fcc (100) with bcc [001] parallel to fcc [011], with parallel oriented square nets in contact. Misfits for magnetic or nearly magnetic 3d-metals on homosymmetric epitaxial substrates are given in table 2. For appropriate misfit definitions and epitaxial orientations in heterosymmetric epitaxial systems compare the extended discussion of fcc (111) on bcc (110) metals given by Bauer and van der Merwe (1986).

The misfit to the substrate can be accommodated in the growing film by elastic strain or by misfit dislocations, which have been first discussed by Frank and van der Merwe (1949) and reported by Matthews (1975b). A schematic representation of an interface between misfitting crystals, resolved into a sequence of edge-type misfit dislocations, is shown in fig. 1. The periodic elastic strain is virtually restricted to a sheet the thickness of which equals roughly the distance of dislocations, p . By simple geometric arguments, p is connected with the in-plane atomic distances a in the substrate and b^* in a growing film by

$$p = ab^*/(a - b^*). \quad (2.2)$$

b^* represents a mean value, which may differ from the bulk lattice parameter if part of the misfit is accommodated by elastic strain in the growing film. For small misfits, it may be energetically favourable for the film to accommodate completely to the substrate by elastic strain, without any dislocations, forming what is called a *pseudomorphic film*, in which all film atoms occupy substrate positions in the plane. The elastic energy of a pseudomorphic monolayer is proportional to f^2 , whereas the dislocation energy of the misfitting monolayer is proportional to the density of dislocations, which means to f . Therefore there is a *critical misfit*, below which the monolayer is pseudomorphic. Being of the order of 10% in general, the magnitude of the critical misfit is larger for $f < 0$, where the film is under expansive strain. It is smaller for $f > 0$, where the film is under compressive strain, as discussed by Markov and Milchev (1984a,b), who showed that this difference results from anharmonicity in the mechanical pair interaction. For thicker films, the critical misfit decreases with increasing film thickness, being roughly proportional to $1/d$. Even above this critical misfit, the accommodation of the misfit is shared between misfit dislocations and some residual elastic strain, as shown, e.g., in fig. 2. Misfit dislocations have been studied extensively by transmission electron microscopy (TEM), cf. Matthews (1975b). For the case of misfits of the order of 10%, the misfit interaction results in periodic misfit