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High Resolution Electron Microscopy of Defects in Materials

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High Resolution Electron Microscopy of Defects in Materials

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High Resolution Electron Microscopy of Defects in Materials

Preface

This volume represents the majority of papers presented at the Symposium on High Resolution Electron Microscopy of Defects in Materials, held at the 1990 Spring MRS Meeting, San Francisco. Generous financial support was provided by International Scientific Instruments (ISI), Japan Electron Optical Limited (JEOL), Philips Electronic Instruments and V.G. Microscopes.

The philosophy of the symposium was to examine the new information which could be provided about defects in materials using HREM and related techniques. It was thought that a more detailed analysis could be provided at this meeting compared to the forthcoming International Congress on Electron Microscopy. There was a high degree of international participation, with scientists from Australia, Belgium, China (Taiwan), France, Germany, Holland, Japan, Mexico, Sweden, Switzerland and the United States. The symposium comprised five oral sessions and one poster session. To a large extent, the proceedings follow the sequence of the meeting itself. As can be appreciated herein, the quality of the work presented was extremely high and we feel that it accurately reflects the advances and contributions made by this field in recent times.

We received much encouragement and cooperation from the symposium participants, including notably the authors, session chairs, speakers, reviewers, the projectionist and the general attendees. We appreciate the opportunity to include the symposium within the MRS Conference itself and we would like to thank the MRS staff, the MRS Conference chairs, our secretaries and colleagues, and our sponsors for much assistance in this collected work.

Robert Sinclair
David J. Smith
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June 1990

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PART I

Metals

INTERDIFFUSION IN METALLIC LAYERS

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ABSTRACT

The atomic structure of ion-sputtered Fe/Ti multilayers with an average composition $FeTi_2$ is studied by high resolution electron microscopy. A systematic use of diffractometry is made to measure the local parameter change as well as to recognise the crystalline phase. Local lattice parameter changes are attributed to compositional changes indicating interdiffusion at a scale of 1.8 nm. The phases are very dependent on the multilayer period, Λ. For small periods, $\Lambda < 4$ nm, the layers are amorphous. For intermediate periods 4 nm $< \Lambda <$ 8 nm the Ti-rich layer is crystalline. And for larger periods both the Fe-rich and the Ti-rich layers are crystalline. These observations are explained in terms of a growth model, assuming a constant depth of mixing during sputtering.

INTRODUCTION

Magnetic multilayers have been recently the subject of active research. The interest for the fundamental understanding of 2D-magnetism as well as for studying the magnetic coupling between parallel magnetic layers has attracted attention for making artificial model objects. For that purpose the production of sharp interfaces between magnetic and non magnetic materials is critical. A nearly perfect epitaxial growth is possible by molecular beam epitaxy [1][2]. Similarly few monolayers of cobalt sandwiched by gold were obtained by evaporation [3] as well as modulated multilayers containing FeNi or Co [4]. On the other hand, magnetic artificial lattice films have been proposed as an appropriate material for magnetic recording head. For that purpose small microcrystals of a high permeability material, such as Fe, are essential [5]. Ion beam sputtering is for that purpose perfectly adequate as it produces small crystallites of the order of the layer thickness. However the main problem which arises from sputtering is an increased mixing of the materials. Recently Dirne et al. [6] have evidenced by Mössbauer spectroscopy and magnestriction measurements that indeed this interdiffusion could be observed. The effect of deposition parameters on the interface structure has been studied by several authors [7][8]. In some systems as Ti/Ni sputter-deposited films of high quality could be obtained at low deposition pressure. However even in this case intermixing is present. For Fe/Ti multilayers the solubilities of one species into the other are rather limited : respectively 0.04 % in α-Ti and 10 % in α-Fe. In addition the diffusion at room temperature is negligible so that deposition mixing should be induced only by direct impact or by radiation enhanced diffusion. The present Fe/Ti multilayer stuctures have an average constant composition $FeTi_2$ but a variable period length from 1 to 50 nm. These layers were studied in detail by X-ray diffraction and Mössbauer spectroscopy [9]. Several typical values of the total period were selected for the high resolution electron microscopy (HREM) which is reported in the present work.

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HREM APPLIED TO INTERFACES

The study of grain boundaries and recently of more general interfaces by HREM has been the subject of many experimental as well as theoretical works [10]. The latest generation of intermediate voltage microscopes gives the exciting prospect of resolution limits below 0.2 nm. The principle of any interface observation is to observe both crystals at each side of the interface along a zone-axis with the interface seen end-on. This geometry provides atomic columns well aligned along the observation axis on either side of the interface, giving an interpretable 2-D projection of a 3-D object. The interpretation, even for such a simple geometry , is rarely direct and a comparison with computer simulated images is usually necessary. However a direct read-out of the structure can be made providing the following conditions are fulfilled: i) the projected distances between atomic columns are always greater than the Scherzer resolution limit, ii) the specimen thickness is smaller than half the main extinction lengths along the axis of observation, and iii) the defocusing distance is close to the Scherzer defocus.

In addition, from the structural information directly available on a HREM image, some chemical information can be deduced. That type of information relies on the a-priori knowledge one has for the particular case under study. For instance, the atomic radii differences between two components will change the lattice parameter in a given way. By applying the Vegard law or an experimentally determined relationship one can relate the measured local lattice parameter with the local composition. This method will be applied in the present work. A second method relies on the difference in the atomic scattering factors. Annular dark field in the STEM mode imaging is directly sensitive to the average composition of the atomic column [11]. HREM images can be also chemically sensitive by an appropriate choice of the thickness and the defocusing distance particularly in compound semiconductors [12]. Moreover the symmetry of the projected structure can be determined directly from an HREM image: it is easy, for instance, to distinguish between a bcc and a hcp structure, particularly when several projection axes are available. The polycrystalline specimens which are studied in the present work are particularly suitable for a statistical study : several projection close to a low index axis are generally available on the same picture. As a consequence the epitaxial relationship, if there is any, can be determined even in a polycrystalline specimens provided the grain size is larger that the specimen thickness. Several metallic multilayer systems were studied by HREM using one of the above-mentioned methods [13 - 15] .

EXPERIMENTAL CONDITIONS

The Fe/Ti multilayers were grown by triode dc-sputtering with alternate deposition of iron and titanium layers on a water (or liquid nitrogen)-cooled (100)Si wafer. Cross-sections were examined in a JEM 4000EX with a Scherzer resolution limit of 0.16 nm at 400 kV. Within this limit the <100>, <110>, and <111> zone axes are directly interpretable. In the hcp-Ti the <0001>, <$2\bar{1}\bar{1}0$>, <$1\bar{2}\bar{1}3$>, <$01\bar{1}0$>, and <$24\bar{2}3$> axes are accessible as well. The variation of the lattice plane d-spacings can be measured by optical diffractommetry. The HREM images are

mounted on an optical bench and illuminated with a ruby laser. The power spectrum of a given plate is recorded and gives an optical diffractogram of a given selected area. These diffractograms provide the local projected crystal structure and the average local lattice parameter. The accuracy of the d-spacing measurements is of the order of 0.2-0.3 % for areas larger than 1x10 nm^2. The silicon lattice image serves as an internal calibration.

CHARACTERIZATION OF THE DIFFERENT PHASES

As it is commonly observed in metallic multilayer structures there is a sudden loss of long-range crystalline order as the bilayer periodicity, Λ , is decreased (for a review see [16]).

For Λ < 4 nm the multilayer is close to an amorphous state although a modulation in composition is visible by X-ray diffraction as well as by HREM.

At intermediate periodicity, 4 nm < Λ < 8 nm, the multilayer is composed of an alternate stacking of amorphous-like layer followed by a crystalline layer (figure 1). At Λ = 7.3 nm, the respective thicknesses of crystal/amorphous part is 4 nm/3.3 nm at room temperature and 3.6/3.6 nm at liquid nitrogen temperature . The deposition order onto the silicon substrate allows to attribute the crystalline part unambiguously to the Ti-rich phase (figure 2). Most of the crystalline grains could be attributed to the metastable bcc-Ti. For instance square pattern diffractograms or images (figure 3) are often observed and cannot be due to the hcp-phase. Few grains are exceptionnaly identify as the hcp-phase and always with the c-axis parallel to the growth axis. The d-spacing is always smaller than the pure Ti whatever is the phase. For instance d_{011} in the bcc-phase varies from 0.226 nm to 0.234nm (corresponding to pure Ti) with an average value around 0.231 nm. This indicates a bcc-Ti metastable solid solution containing Fe. A strong texture is apparent from the electron diffraction or from the HREM images. At room temperature the bcc phase is strongly oriented with its <011> axis parallel to the growth axis. The angular divergence of the texture is limited to 3.5^0 at room temperature and to 11^05 at 77 K. The average crystallites size is of the order of 4 nm.

For periodicity larger than 8 nm (defined within 0.2 nm), the Fe-rich layer becomes also crystalline as illustrated on figure 4. The layer thicknesses are respectively 3.5 nm and 6.5 nm for Fe and Ti-rich parts. The crystalline Fe-rich is bcc and the Ti-rich layer is mainly hcp. The c-axis has two preferential orientations: either along the growth axis (designed as the A-texture) or perpendicular to it with $<01\bar{1}0>$ along the growth axis (B-texture). The crystallites sizes are equal to the full layer thickness but are extended in the layer plane over distances two or three times larger.

For multilayer periodicity larger than 10 nm and particularly at Λ=47 nm alternate layers of crystalline bcc-Fe and hcp-Ti are observed (figure 5). Far from the interface the d-spacings correspond to the bulk values for pure materials. The thicknesses are in the expected ratio 1:3 for the average composition $FeTi_2$ and the respective atomic volume (2:3 ratio). In hcp-Ti the texture is a mixture of A and B. In bcc-Fe the texture is always with the <011> axis parallel to the growth axis. In