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Recent advances in molecular beam epitaxy of metallic multilayers and superlattices

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Résumé. — Dans cet article de revue, nous présentons quelques résultats récents obtenus en épitaxie par jets moléculaires de multicouches et super-réseaux métalliques. Après une brève description de la physique de ces structures multicouches, nous concentrons notre discussion sur les spécificités techniques de l'épitaxie par jets moléculaires de métaux ; en particulier, nous discutons le problème de l'évaporation à haute température. En comparant les résultats de croissance obtenus sur les systèmes multicouches Ag/Fe et Fe/Cr, nous mettons en évidence l'influence de la nature des métaux mis en jeux sur la qualité finale des super-réseaux.

Abstract. — We present a review of some recent results obtained in molecular beam epitaxial growth of metallic multilayers and superlattices. After a brief description of the physics of these multilayer structures, we focused on specific developments of the metal M.B.E. technique including a discussion on high temperature evaporation. By comparing the growth characteristics of the Ag/Fe and Fe/Cr multilayer structures, we emphasize on the influence of the nature of the metals involved in the superlattice structure on its overall quality.

1. Introduction.

Metallic multilayers (M.M.) are thin films in which the composition is modulated by alternating deposition of different metals. The term metallic is used to make a distinction with semiconductors multilayers. If the atomic planes of the M.M. structure are coherently stacked, one use to label the material as a «superlattice» whereas if this additional ordering is absent, the term «multilayer» is used.

During the last few years, the study of M.M. have emerged as a very promising field from both fundamental and technological point of view [1]. This is partly because owing to the development of sophisticated thin film growth techniques such as Molecular Beam Epitaxy (M.B.E.), it is now possible to produce high quality single-crystal metallic superlattices of reasonably matched metallic materials. Moreover, the specific development of metal M.B.E. technique can be understood as a consequence of the large area of potential applications that offer the metallic multilayers, which leads this field to be an important industrial challenge.

In this brief review, we will describe some specific aspects concerning the M.B.E. growth of metallic multilayers. In section 2, we present the general background of the physics of these M.M. structures. A large list of M.M. systems for several fields of application can be found in reference [2]. In section 3, we discuss some bulk properties of the involved metals and their influence on the growth of M.M. One consequence of this is the necessity, in most cases, for high temperature evaporation. As far as this is the origin of the main evolution of the metal M.B.E. technique as compared to standard M.B.E., we will describe in section 4 the various solutions that have been adopted. Finally, section 5 is devoted to the growth of M.M., including nucleation problems, growth modes and interface quality.

The association of metals in thin multilayer structures is suitable for the study of physical properties which depend on characteristic lengths. The basic parameters in superconductivity, such as the coherence length or the transition temperature, can be strongly influenced by the variation of the thickness of the layers in a multilayer design [2-4]. However, it should be noted that the total amount of people that are currently working on metallic multilayers for superconducting applications have considerably decreased since the discovery, in 1987, of high-$T_c$ superconductors.

Multilayers are also produced as X-ray [5] and neutron mirrors [6]. Multilayers consisting of two metals with a large difference in refractive index are indeed of interest for tailoring specific optical properties. Such multilayers offer new opportunities for fabricating X-ray optical elements. In this field of optic applications, the quality of the interfaces is obviously of crucial importance.

The interest of M.M. covers other fields such as mechanical properties. In this context, one of the most spectacular property is the so-called super-modulus effect which corresponds to a strong variation of the Young's modulus due to the multilayer arrangement. Such effect has been observed in particular for Au/Ni, Cu/Pd, Ag/Pd and Cu/Au systems [7] where the Young's modulus was found to be more than two times higher than in the corresponding alloys [8].

The interest in the magnetic properties of multilayers in which one of the material is magnetic in its bulk form, concerns several effects. Here we choose to describe the two main ones, as far as they can lead to important technological applications.

First of all there are interface effects depending on the kind of material that is neighbouring the magnetic layers. The main one is that the anisotropic environment at the interface can strongly influence the preferential direction of the magnetization in the magnetic layers. For example, in Ag/Fe superlattices, it has been found that, for thickness $t_F$ of the individual Fe layer below 10 Å, this interface anisotropy overcomes the dipolar effects, i.e. the so-called demagnetizing field effect [9]. This strong uniaxial anisotropy induces, for $t_F < 10$ Å, a preferential direction for the magnetic moments perpendicular to the plane of the layers. This effect have now been observed in several M.M. systems [10]. These multilayers with strong perpendicular anisotropy are of particular interest for application in high density magnetic recording.

Another source of interest is the long-range coupling between neighbour magnetic layers across the non-magnetic ones. This can lead to various magnetic superstructures in the material. For example, an antiferromagnetic coupling have been found in Gd/Y superlattices [11] while an helimagnetic coupling was found in Dy/Y superlattices [12]. For these Rare Earth systems, the coupling were ascribed to a R.K.K.Y.-type mechanism [13]. Interlayer couplings have also been found in some transition metal multilayers [10], like for example an antiferromagnetic coupling in Fe/Cr multilayers [9, 14, 31].

3. Some general considerations about materials involved in metallic multilayer elaboration.

In table I, we present data concerning some typical transition or Rare Earth metals that are used as multilayers components. We first indicate the evaporation temperature corresponding to a vapor pressure of $10^{-3}$ torr. Generally, this value allow to obtain a typical growth rate of 1 Å/s. It can be seen from these data that, in most cases, one have to heat at higher temperatures than the maximum required with standard M.B.E. Knudsen cells (typically 1 250 °C). In the next section, we will discuss the different technical solutions that have been adopted to obtain sufficiently high fluxes of these refractory materials.

Table I. — Data of interest in M.B.E. of some metals involved in multilayers. $T_e$ is the evaporation temperature corresponding to a vapor pressure of $10^{-3}$ torr [32].

<table>
<thead>
<tr>
<th>Metals</th>
<th>Fe</th>
<th>Cr</th>
<th>Ag</th>
<th>Gd</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_e$ (°C)</td>
<td>1342</td>
<td>1267</td>
<td>922</td>
<td>1192</td>
<td>1467</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>bcc</td>
<td>bcc</td>
<td>fcc</td>
<td>hcp</td>
<td>hcp</td>
</tr>
<tr>
<td>Lattice parameter (Å)</td>
<td>2.866</td>
<td>2.885</td>
<td>4.086</td>
<td>$a = 3.636 , c = 3.647$</td>
<td>$a = 5.783 , c = 5.731$</td>
</tr>
</tbody>
</table>

In table I, we have also indicated the crystal structure and lattice parameters of these metals, in standard temperature and pressure conditions. These two informations, for both components of the multilayer, will influence the choice of the substrate in terms of lattice matching. However, one have also to take into account the possible chemical reactivity between the substrate and the overlayer metals, which could lead to the necessity of growing a suitable heteroepitaxial buffer layer between the substrate and the multilayer structure.

For example, Gd/Y and Dy/Y rare-earth superlattices were grown by M.B.E. on (1120) Al$_2$O$_3$ substrates. It was found that Rare Earth oxides were
incorporated during growth by chemical interactions of the Rare Earths with oxygen atoms supplied from sapphire. This difficulty was circumvented by inserting a (110) Nb chemical buffer layer which does not react with Rare Earths or with the sapphire substrate [15].

In the field of transition and noble metal multilayers, GaAs have been the most extensively studied substrate [16, 17]. The main reasons are the relatively small lattice mismatches between GaAs and the overlayer metals (Fe, Cr, Ag, Au, ...), and the fact that M.B.E. technique allows to prepare highly perfect (001) GaAs surfaces. Moreover, an exciting challenge would be to combine magnetic multilayers and semiconductor structures in order to integrate on the same semiconductor wafer electronic and magnetic functions.

The choice of the substrate can be also influenced by the purpose of stabilizing a metastable phase of the metallic overlayer [18]. Indeed it is one of the most intriguing aspects of epitaxial growth. For example Maurer et al. have succeeded in the growth of Fe/Ru superlattices in which the Fe crystallizes in an h.c.p. structure, provided that the Fe layer thicknesses does not exceed 12 Å [19]. These structures are of great interest since the magnetic properties of iron are predicted to change dramatically upon changing the crystal structure and interatomic distances.

4. Specificity of the metal M.B.E. technique.

In metal M.B.E., the importance of ultra-high vacuum environment is not so crucial as in III-V M.B.E. technique, where one must control the purity of the grown sample on a low dopant level scale. However, when evaporating metals such as Fe or Cr, an improvement of the pressure is found, which is due to a strong gettering effect. For this reason, the pressure during growth is often as low or even lower than the base pressure of the system (typically 10⁻¹⁰ torr).

We now proceed with the problem of high temperature evaporation. Three different types of solutions have been adopted to solve it. First of all, it should be noted that standard Knudsen cells with pyrolytic boron nitride crucibles can reach a maximum temperature of ~1 250 °C. Above, it is well known that significant decomposition of the crucible occurs. In spite of these considerations, several groups have used such cells to evaporate iron [16], thus being limited in the obtainable flux and growth rate.

Up to now, in most cases, people have used electron beam guns to evaporate the refractory metals. Then it was necessary to build specially designed M.B.E. systems in order to incorporate the e-beam evaporation technique [15]. Basically, the electron beam guns consist of an open crucible, the electron beam being directly focused on the source material by a magnetic field. An advantage of the e-beam technique is that it allows to evaporate almost any kind of material. One disadvantage of this technique is that there is no way of controlling the temperature of the source material. Thus it is necessary to couple this technique with an accurate deposition control and shutter monitoring; generally quartz monitors are used for this purpose but a more sophisticated technique based on optical emission have also been developed [15].

We have developed a third solution which is a combination of the two other ones in the sense that it is a Knudsen cell where heating is achieved using electronic bombardment of a metallic crucible [20, 21]. A scheme of this « high temperature » cell is represented in figure 1.

![Fig. 1. — Scheme of a high temperature cell heated by electron bombardment for metal M.B.E. growth.](image)

5. Growth of metallic multilayers.

A number of recent experimental studies have shown that molecular beam epitaxy is able to produce high quality single-crystal metallic multilayer structures [15, 16, 19, 22]. However, the structural perfection of the multilayered films is obviously critically dependent on the nature of the materials involved in the structures. In particular, the development of superlattices with sharp interfaces depends on the interplay of thermodynamics and kinetic processes which govern both the interfacial diffusion and the growth mode of the considered materials. One of the main difficulties of growing highly perfect multilayers arises from the fact that each material acts alternatively as the
deposit and the substrate, situations which are not in general energetically equivalent and depend on their basic thermodynamical properties (in particular the difference between their surface free energies [23]). In order to impose a favorable growth situation (i.e. not too far from the ideal layer by layer growth mode) while preserving the single-crystal nature of the multilayer, the experimenter action will be then to select growth parameters giving rise to a suitable balance of kinetic and thermodynamic effects. It is still more difficult to overcome problems due to strain effects arising from the lattice parameter difference between the materials involved in the superlattice. This point severely limits the number of metal pairs which can be successfully used to build a high quality superlattice structure on a given substrate. It remains from these basic considerations that it is in general not easy to grow highly perfect single-crystal metallic superlattices even by using a powerful technique such as M.B.E.

The aim of this section is to briefly illustrate the influence of the nature of the metals involved in the superlattice structure on its overall quality, by comparing the M.B.E. growth of two typical systems: Ag/Fe and Fe/Cr on (001) GaAs substrate.

5.1 Ag/Fe SUPERLATTICES. — The Ag/Fe system is a typical example of systems for which superlattices with high interfacial quality can be grown on (001) GaAs providing that the critical steps controlling the growth process are correctly taken into account. The first important step before growing any metal structure on top of a (001) GaAs substrate is to grow an homoepitaxial GaAs buffer layer in order to improve the smoothness of the substrate surface. This is because the details of the nucleation of the very first metal atoms impinging the surface are critically dependent of the defects present on the surface. The development of a smooth and well ordered surface is therefore necessary to correctly initiate the first metal layer growth. Moreover, beyond the first few deposited monolayers, the quality of the starting surface influences the overall structural quality of the multilayer. The GaAs homoepitaxial buffer layer is grown in standard M.B.E. growth conditions [24]. When obtaining a smooth reconstructed (001) GaAs surface, a subsequent step which has been proven effective in growing high quality superlattices [16] is the growth of a metal buffer layer. In the case of Ag/Fe superlattices, this step is mainly performed in order to relax the strain associated with the lattice mismatch between (001) Ag or (001) Fe and (001) GaAs (2.2 % and 1.4 % respectively). However, with the aim of studying the magnetic properties of the final superlattice structure, a thick buffer layer of Fe is clearly undesirable. On the other hand, the growth of a Ag single-crystal buffer layer on (001) GaAs is somewhat difficult because two different epitaxial relationships exist leading to (001) or (001) Ag orientations [25, 26]. This problem is a consequence of the strong anisotropy of the (001) GaAs surface [22] and can be overcome by first depositing a thin layer of Fe, which only presents the (001) orientation, before growing the Ag layer [27]. On top of this Fe nucleation layer, the growth of (001) Ag in the 200-400 K range occurs following a two dimensional (2D) layer by layer growth mode as indicated by the observation of reflection high energy electron diffraction (RHEED) intensity oscillations when the growth is reinitiated after roughly 20-50 Å have been deposited (Fig. 2) [22]. However, in the same temperature range, no RHEED intensity oscillation is observed neither for the growth of (001) Fe on (001) GaAs nor on (001) Ag. This is presumably due to the difference in surface diffusion coefficients of the two metals. According to Flynn [28], the lower limit of the growth temperature below which the roughening of the growth front occurs is related to the melting temperature of the metal, as the surface diffusion coefficient is. Considering that the melting temperature of Fe is more than 500 K above the Ag one, it can be inferred that in the 200-400 K range the surface diffusion of Fe atoms is insufficient to give a smooth growth front. However, the growth temperature cannot be significantly increased without provoking strong interfacial diffusion which severely degrades the superlattice structure. Nevertheless, even for the low temperature range imposed by interdiffusion effects, the RHEED pattern obser-
vation during the growth of a Ag/Fe superlattice indicates that the growth is not too far from the ideal layer by layer mode. This is confirmed by X-rays diffraction analysis performed on those superlattices. Figure 3 shows a spectrum obtained in the $\theta$-2$\theta$ geometry on a Ag (34 Å)/Fe (14 Å) superlattice [30]. Several satellites are observed around and between the (002) reflection of Ag and Fe, which, in first approximation, is a signature of the interface quality. Indeed, interfaces act on the satellite peaks as an effective Debye-Waller factor; so we can only observe a large number of satellite peaks if the interfaces are sufficiently sharp. It seems therefore that the two types of interfaces in the Ag/Fe superlattices are abrupt. In all the spectra, the intensity of the (004) GaAs peak is small because there is no coincidence between the (001) axes of Ag, Fe and GaAs. This point has been studied in details by Farrow et al. [27] and has been ascribed to a coherency strain and tilted epitaxy of the superlattice.

5.2 Fe/Cr MULTILAYERS. — Recently, it has been shown that Fe/Cr multilayers can also be grown on (001) GaAs [17]. Furthermore, these multilayers exhibit, for sufficiently thin Cr layers (typically below 30 Å) very exciting giant magnetoresistance properties [20, 21, 28]. This new effect, which suggests interesting potential applications in the field of sensors, has been ascribed to spin-dependent transmission of the conduction electrons between Fe layers through Cr layers [28]. However, the structural quality of Fe/Cr multilayers is far from being as good as the one usually achieved in the Ag/Fe system. Actually, the problem is that, even if the first growth periods of the superlattice exhibit RHEED patterns characteristic of sharp interfaces and a fairly good single crystal growth, a slight but continuous degradation occurs when the growth proceeds, and become clearly observable above roughly 300 Å of deposition. It is in fact almost impossible to grow superlattices beyond 1 500 Å while keeping the single-crystal nature of the structure. These superlattices were obtained by growing first a thin Fe layer on (001) GaAs, as it is usually done in order to impose a (001) orientation for the entire structure [17]. If Cr is first grown on (001) GaAs, it takes a (112) orientation. Cr/Fe multilayers have been grown following this orientation with the aim of comparing their structural properties to those of (001) oriented structures. No clear improvement was observed.

As a first attempt to improve the crystallinity, a thick (relaxed) In$_{0.28}$Ga$_{0.72}$As buffer layer has been used in order to reduce the strain between GaAs and the superlattice. The lattice parameter of this alloy is identical to that of two unit cells of bcc Fe [29]. No significant improvement has been found. Similar results are also obtained when a 500 Å thick (001) Ag buffer layer is used. Up to now, the only parameter which has been proven effective in controlling the structural quality of the Fe/Cr multilayers is the growth temperature. After a superlattice growth of 1 200 Å (20 periods), the Fe RHEED pattern, as well as the Cr one, markedly depends on the growth temperature: below roughly 300 K rings are formed indicating a rather polycrystalline growth, while around 350 K the single crystal growth is still prevalent [30]. However, above 400 K faceting effects occur indicating that the growth is becoming largely three dimensional.

Conclusion.

In conclusion, this brief review of recent results in the M.B.E. growth of metallic multilayers shows that the development of specially designed systems opens now the possibility of fabricating high quality single-crystal metallic superlattices. In most cases, this is only possible while controlling a high temperature evaporation technique for refractory materials. Concerning the growth of these multilayers, one have to keep in mind the two following features that are quite specific to metals, as compared with semiconductor compound technology. First, the growth temperature is generally much lower, typically between room temperature and 200 °C. Consequently, the growth rates should also be lower, typically around 0.1 Å/min. The structural properties of the final structure mainly depend on the nature of the metals involved, and not only on their lattice parameters. In each case, one have to optimize the growth parameters in order to develop sufficiently well defined multilayer structures for the analysis of their physical properties as well as for device applications.
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