Electron beam evaporation of oriented Nb films onto GaAs crystals in ultrahigh vacuum

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Thin layers of Nb, 100–400 Å thick, were grown by electron beam evaporation on (100)GaAs substrates in a molecular beam epitaxy system. The crystallographic relationship between deposit and substrate was monitored in situ by reflection high-energy electron diffraction, and after deposition by transmission electron microscopy and grazing-incidence x-ray diffraction. In spite of the large lattice mismatch (17%) and the low deposition temperature (40–400 °C), a quite well oriented deposit with the orientation (100)Nb∥(100)GaAs and [001]Nb||[011]GaAs was obtained for a substrate temperature of ~170 °C. Changing the substrate temperature from the optimum value of ~170 °C in either direction resulted in a gradual deterioration of the epitaxy.

The importance of metal-semiconductor junctions has steadily increased because of their use in a large variety of electronic and optoelectronic devices. This technological effort has been followed by a scientific effort to characterize and understand the metallurgical and electronic properties of metal-semiconductor interfaces. One of the recent, more interesting aspects of metal-semiconductor studies is the case of metals growing epitaxially on III-V compound single-crystal substrates. Such structures have both technological and scientific interest. An important example is the implementation of the metal-base transistor. This structure requires the growth of a single-crystal metal layer on a semiconductor substrate, on which in turn an epitaxial semiconductor layer can be deposited. In the case of GaAs, the substrate material in this study, some face-centered-cubic (fcc) metals with a good lattice match, such as Al or Au, have been shown to grow epitaxially on it. However, the high reactivity of these metals on GaAs at relatively low temperatures may result in chemical reaction at the interface, during growth or subsequent heat treatment, that might affect the junction properties. The only body-centered-cubic (bcc) metals, that have been shown to grow epitaxially on GaAs, are iron and a metastable bcc phase of cobalt. Both metals were grown on a cleaved GaAs substrate, with the orientation (110)bcc∥(110)GaAs and [001]bcc||[001]GaAs. The relatively low misfit of 1.35% (for α-Fe/GaAs) assures good lattice matching. An interesting issue is the possibility of epitaxy in the absence of lattice matching between substrate and deposit. Such a problem has recently been addressed by Grovenor et al. who studied the epitaxial relationship between fcc metal substrates and various bcc metal deposits. They found that the films grew with three different epitaxial orientations, each of them occurring in a particular range of lattice parameter ratio. In addition, calculations of the misfit showed that for each range the observed epitaxial orientation has the lowest strain energy.

Epitaxial growth of two bcc metals, molybdenum and tungsten, that have a large lattice mismatch with GaAs, has recently been tried in ultrahigh vacuum at substrate temperatures $T_s \leq 500$ °C which are low relative to the melting point of the deposits. It was found that at temperatures between 200 and 450 °C very small crystallites of Mo grew epitaxially with their (111) plane parallel to the (100)GaAs. The quality of the deposit could be improved when (111)GaAs substrates were used, Tungsten, on the other hand, could be grown on (100)GaAs substrates at this temperature range only as a randomly oriented polycrystalline film. The epitaxial growth of Mo on (100)GaAs at such low deposition temperatures in spite of the large mismatch, and the fact that its epitaxial relationship was not covered by the rules found by Grovenor et al., stimulated the present study on deposition of niobium thin films on (100)GaAs.

Niobium was deposited in a Riber 1000-1 molecular beam epitaxy (MBE) system, with a residual gas pressure during deposition of $5 \times 10^{-10}$ Torr. First, a GaAs epilayer, ~1 μm thick and doped with Si ~1 x 10$^{17}$ cm$^{-3}$, was grown on an n $^+$ (100)GaAs substrate at 600 °C. Then the sample was rotated away from the effusion cells, and its temperature was gradually reduced to the desired substrate temperature for the metal growth, $T_s$. After waiting ~3 h, to minimize the As background pressure, a thin niobium layer, with a thickness ranging from 100 to 400 Å, was deposited by a 5-kW electrostatic electron gun evaporator, especially designed to minimize the escape of stray electrons that can cause impurity desorption from the walls. To minimize background impurities, the deposition rate was kept low at a rate of 1 Å/min for the first 50 Å of Nb; in some cases it was then increased up to 4 Å/min. The substrate temperature was varied in the range from 40 to 400 °C to study its effect on the deposit microstructure.

The characterization of the films was focused mainly on their microstructure and their orientation relationship with the substrate. In situ analysis was performed by reflection high-energy electron diffraction (RHEED), which is monitoring the crystallography of the top few atomic layers during growth. After deposition, the samples were analyzed outside the MBE system by transmission electron microscopy (TEM) and by grazing-incidence x-ray diffraction (GID), a surface-sensitive technique developed recently by Mara et al. With the latter technique, crystallite size and strain can be determined parallel to the interface from 2θ-θ scans. To establish the substrate/epitaxial orientation relationship, the detector was fixed at the diffraction angle 2θ$_{hkl}$ for the film.
and the sample was rotated around the surface normal in a so-called ω-scan. GID allows nondestructive characterization of the bilayers, whereas for TEM characterization the substrates had to be thinned from the back by chemical etching.

In situ observation by RHEED of the (100) oriented epilayer of GaAs, prior to the niobium deposition, showed the surface to be (4×6) reconstructed in most of the cases. For a few samples the As-stabilized (2×8) reconstruction was observed. Immediately upon the onset of the metal deposition, the surface reconstruction pattern disappeared, and only the bulk pattern of GaAs was observed up to a deposition thickness of ～5 Å. This allows us to deduce that our results relate to the Nb/unreconstructed (100) GaAs interface. During deposition of the first layers of Nb (～20–30 Å), the screen showed only diffuse scattering. Thereafter, a diffraction pattern appeared for substrate temperatures T_s < 270°C. A similar initial transition region was also observed for Mo deposits, and we presume that this indicates that crystallization of the deposit occurs only after this critical thickness has been reached

The RHEED pattern observed in the substrate temperature range from 100 to 270°C consists of broad spots from Nb suggesting that the deposit consists of small, possibly strained crystals and is continuous, and it indicates an epitaxial relationship of (100)Nb||(100)GaAs and [001]Nb||[011]GaAs. For T_s < 100°C only blurred rings were observed indicating randomly oriented fine-grained polycrystalline growth, while for 270°C < T_s < 400°C no pattern could be observed at all after the disappearance of the GaAs substrate pattern.

More information about the microstructure of the deposit and its relationship to the substrate was obtained by TEM. In Fig. 1 the diffraction pattern is shown for a sample deposited at T_s = 170°C which had the best epitaxial quality. In addition to the substrate diffraction spots, elongated arcs corresponding to the Nb film can be observed. The fourfold symmetry of the substrate and film diffraction pattern confirms the orientation relationship already established in situ by RHEED. The occurrence of continuous rings in the Nb diffraction pattern indicates the presence of some randomly oriented crystallites. The form of the Nb diffraction rings suggests that the crystallites aligned with the substrate are small and have a mosaic spread of ～±10° about the exact epitaxial orientation. A (011) dark field TEM image of the aligned Nb crystallites is shown in Fig. 2, revealing small oriented grains, ～200 Å in size, that are embedded in a nonoriented matrix. From Fig. 2 the proportion of epitaxially aligned crystallites is probably underestimated, since some of the aligned crystallites may not be imaged because of bending during the specimen preparation and observation. A gradual decrease in the intensity of the maxima in the Nb diffraction pattern was observed as the substrate temperature T_s during growth was either decreased or increased from the optimum T_s = 170°C, confirming the results obtained in situ by RHEED. In the same temperature range, on (111) GaAs substrates, Nb films grew also with a (100) plane parallel to the interface, but with less well-developed orientation, as evidenced by RHEED and TEM.

X-ray diffraction patterns of the Nb films were recorded by GID in 2θ-θ and ω-scans. Figure 3 shows ω-scan data of the (011) reflection of Nb for three different deposition temperatures, T_s = 40, 170, and 270°C. The pattern of Fig. 3(b), with T_s = 170°C, confirms the orientation relationship found by RHEED and TEM. The orientational spread is rather large, as indicated by the half-peak-intensity width of Δω ~ 11° and 8° for the films with a thickness t = 400 and 120 Å, respectively. In another film, grown also at T_s = 170°C, but with a thickness of only ~120 Å, a lower value of Δω ~ 8° was measured. It is noted that, while for T_s = 270°C a much smaller proportion of the crystallites are still aligned, for T_s = 40°C the deposit is practically randomly oriented. The intensity fluctuation observed in the top pattern, and also to some extent in the bottom one, is probably an instrumental and sample shape characteristic. The grain size parallel to the interface has been estimated to be D ~ 120 Å for all samples having a nominal film thickness of t ~ 120 Å, independent of T_s. For the sample depicted in Fig.
misfit is relaxed, presumably by formation of misfit dislocations. We note that an in-plane rotation of the Nb mesh by 45° will result in the so-called BN45 epitaxy with about the same mismatch, but opposite in sign, and with the film under compression. Such an epitaxy has not been found in this study. It may be argued that, due to the anharmonic shape of the interatomic potential, film tension is energetically favored over film compression for the same amount of strain, as is indeed observed. This argument applies to the nucleation stage of deposition, before stress relaxation by misfit dislocation generation has occurred. Grovenor et al. reported that for a deposit/substrate lattice parameter ratio of $r < 0.78$ BN epitaxy is prevalent, and that BN45 epitaxy can be obtained only for $r > 0.92$ [in the intermediate range another epitaxy, called A, with (110) bcc || (100) fcc was obtained]. This behavior was attributed to a tendency to minimize the elastic strain energy. For Nb/(100)GaAs, with a lattice parameter ratio of $r = 0.585$, $r$ is beyond the range considered by Grovenor et al. While it might be expected that the BN orientation would be preferred for a range of values of $r$ less than 0.707, the value for zero misfit, the limit of the stability has not been addressed at all until now. It is interesting that the epitaxy of the Nb/GaAs system differs from that of Mo/GaAs since for the latter the orientation relationship (111)Mo||(100)GaAs has been found to be predominant. The GID study of the Mo/GaAs system revealed an extremely weak BN epitaxy component to be present also, suggesting that the lower value of the lattice parameter ratio for that system, $r = 0.557$, is at the transition to still another regime, not considered by Grovenor's rule. It is striking that niobium grows with the (100) plane on both (100) and (111) GaAs substrates, whereas molybdenum prefers a (111) growth plane for both substrates. In both cases, the orientational spread is smallest where the lattice planes parallel to the interface have the same symmetry in film and substrate. Further study seems appropriate.

3(b), with $T_s = 170 \degree$ C and $t \sim 400 \AA$, the estimate for the average grain size is $D \sim 180 \AA$. Small tensile strains parallel to the interface of $e = 0.47, 0.35$, and $0.2\%$ were determined for the samples with $T_s = 40, 170$, and $270 \degree$ C, respectively.

Our results show a variation of epitaxial quality with temperature of deposition. The trend toward randomness with decreasing temperature can be explained by the decrease of diffusivity and is expected. However, the deterioration of epitaxy as the temperature increases above $170 \degree$ C is unexpected. We believe that this behavior can be attributed to a reaction that may have taken place at the interface between Nb and GaAs, possibly involving only a few monolayers. We have observed the extensive formation of the compound NbAs after post-deposition annealing at $440 \degree$ C inside the TEM. This reaction might take place at lower temperatures only at the interface, to an extent sufficient to disturb the registry of the deposit with the substrate.

The epitaxy observed, (100)Nb||(100)GaAs and [001]Nb||(011)GaAs, is well known as the Baker–Nutting (BN) relationship. The lattice mismatch, calculated from the bulk lattice parameters and verified by the diffraction pattern of Fig. 1, has the large value of 17%, causing the film to be under tension, in the absence of relaxation. Most of this

![Graph showing GaAs directions and counts vs. omega](image)

**FIG. 3.** Grazing-incidence x-ray diffraction o-scan data of the (011) reflection of three Nb films deposited on (100)GaAs at different substrate temperatures $T_s$.