Heteroepitaxial growth of ionic compounds between dissimilar crystal lattices

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Heterogeneous growth of CuCl and CuBr, zinc-blende-structure ionic compounds, on (001) surfaces of MgO with rock-salt structure has been studied by a molecular beam epitaxy technique. We found that CuCl and CuBr had two different in-plane epitaxial relationships, CuCl(111)/MgO(001) with CuCl[$1\bar{1}0$] // MgO[110] and CuBr(111)/MgO(001) with CuBr[$1\bar{1}0$] // MgO[100]. This difference is explained by the change in the atomic configurations of the initial nuclei with respect to the substrate lattice arising from a 5% difference in lattice parameter between CuCl and CuBr.

Heterogeneous nucleation followed by overlayer formation has been one of the most informative methods of studying interfaces of two different materials. A heterostructure fabricated from two crystals which differ markedly in crystallographic symmetry and/or lattice constant allows a larger range of the interfacial configuration, and should provide further knowledge about the cohesion at interfaces. In particular, ionic compound growth systems inherently cause a wider range of the crystallographic arrangements in the overlayers than do covalent systems, because of the absence of directional bonds and the smaller cohesive energies.

We have studied the heteroepitaxial growth of ionic I-VII compounds with zincblende structure, CuCl ($a_0 = 0.5406$ nm) and CuBr ($a_0 = 0.5691$ nm), on (001) surfaces of MgO ($a_0 = 0.421$ nm) with rock-salt structure by molecular beam epitaxy (MBE).[1,2] These systems provided completely dissimilar interfaces of CuCl(111)/MgO(001) and CuBr(111)/MgO(001). The crystal growth was performed at a base pressure of 5×10^{-9} Torr in a chamber equipped with a reflection high-energy electron diffraction (RHEED) system. The substrates used here were single crystals of MgO with a polished (001) surface. CuCl and CuBr were evaporated congruently from the respective crystals purified by a zone melting method.

Figure 1 shows RHEED patterns from (a) a 20-nm thick CuCl film and (b) a 20-nm thick CuBr film, grown on MgO(001) at
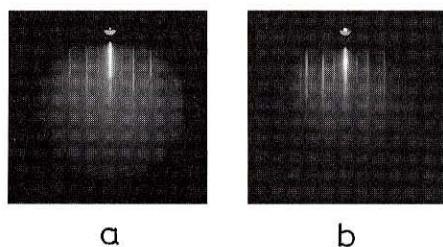
333 K. Both patterns show several well-defined streaks, consisting of two different reflections along the [$1\bar{1}0$] and [$1\bar{2}1$] axes in a (111) plane of the cuprous halides. This indicates that the growing surfaces are two-dimensional. The typical RHEED patterns were observed at different incident azimuths between CuCl and CuBr, $+15°$, $+45°$, $\cdots$ from MgO[010] for CuCl and $+0°$, $+30°$, $\cdots$ from MgO[010] for CuBr. These results show that CuCl and CuBr have two different in-plane orientations with respect to the substrate lattice, and that each system involves several domains with different in-plane orientations. From X-ray diffraction (XRD) ϕ scan results using a four-circle diffractometer as well as the RHEED data, CuCl[$1\bar{1}0$] was found to be parallel to the MgO[110], [$\bar{1}10$], [$\bar{1}\bar{1}0$] and [$1\bar{1}0$] axes, and CuBr[$1\bar{1}0$] to be parallel to the MgO[100], [010], [$\bar{1}00$] and [$0\bar{1}0$] axes. One type of the relationships is illustrated schematically for each system in Fig. 2. The other domains are obtained by in-plane rotations of $n\pi/2$ ($n = 1, 2, 3$).
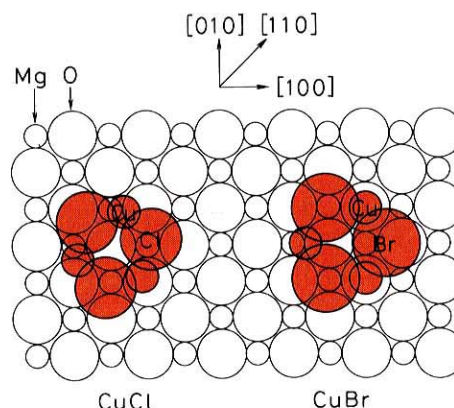

Fig. 2. In-plane crystallographic alignments of CuCl(111) and CuBr(111) grown on MgO(001), shown schematically. The size of each sphere is in proportion to a corresponding ionic radius.

a   b

Fig. 1. RHEED patterns of (a) a 20-nm thick CuCl film and (b) a 20-nm thick CuBr film, grown on MgO(001) at 333 K. The incident azimuths are $+15°$ from MgO[010] for CuCl and $+0°$ from MgO[010] for CuBr.

This in-plane rotation is interpreted qualitatively by the geometrical effects in the atomic configuration of the initial nuclei on terraces of MgO(001) which arise from a 5% difference in

lattice constant between CuCl and CuBr. The surface of ionic crystals is characterized as an ionic corrugation with a periodicity, d_s, corresponding to the distance of two identical ions. Since the Coulomb interaction plays a predominant role in the adsorption of ionic-compound systems,[3] the matching of d_s and a spacing of the same ions in the overlayers, d_{ad}, is a key to determining the atomic arrangement of the initial nuclei with respect to the substrate lattice. For the MgO(001) surface, two kinds of ionic corrugations with $d_s = 4.21$ Å along [100] direction and $d_s = 2.98$ Å along [110] direction are considered. In the configurations as shown in Fig. 2, the respective values of d_{ad} are 3.82 Å for CuCl and 4.02 Å for CuBr. It follows that CuX (X = Cl or Br) with a larger d_{ad} takes an arrangement to fit the 4.21-Å periodicity on MgO(001), leading to the arrangement of CuX[1$\bar{1}$0] // MgO[100]. In contrast, CuX with a smaller d_{ad} prefers to fit the smaller d_s of 2.98 Å, providing the arrangement of CuX[1$\bar{1}$0] // MgO[110]. This tendency agrees well with the present results.

The film morphology was studied by using atomic force microscopy (AFM). Figure 3 shows AFM topographs of (a) a 20-nm thick CuCl film, (b) a 20-nm thick CuBr film, and (c) a 2-nm thick CuCl film. These films were grown on MgO(001) at 333 K. It is clear that separated islands with hexagonal idiomorphic shapes are formed in both systems of CuCl/MgO(001) and CuBr/MgO(001). The directions of the hexagonal-shaped crystals also indicate the 15° (or 45°) rotation in the in-plane crystal alignment between CuCl and CuBr, consistent with the RHEED and XRD results. Although the islanding is observed in the growth of CuCl and CuBr, the (111) overlayers of CuCl and CuBr exhibit a preferential lateral growth, thus resulting in a higher coverage within an early stage of the growth. The observed behavior in morphology depends markedly on the substrate temperature. A lower substrate temperature gives a larger number of nuclei and a more rapid approach to a full coverage, and vice versa.
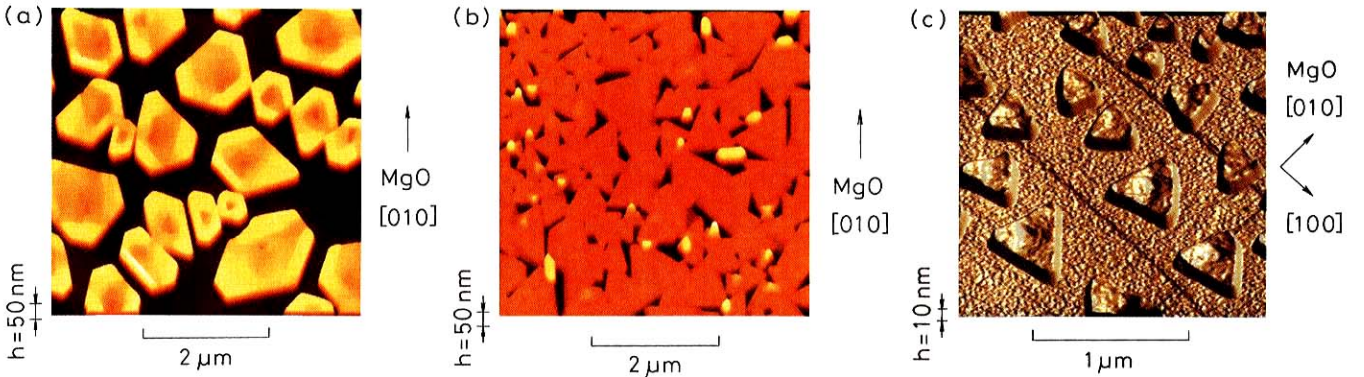

Fig. 3. AFM gray scale images of (a) a 20-nm thick CuCl film and (b) a 20-nm thick CuBr film, grown on MgO(001) at 333 K. (c) AFM topograph modeled with a light source of a 2-nm thick CuCl film grown on MgO(001) at 333 K.

As seen in Fig. 3(c), the steps appearing on MgO(001) are clearly observed simultaneously as well as CuCl hexagonal islands with heights of 7 nm. The straight steps with heights of 0.4–0.8 nm run parallel to MgO[100] or [010] with irregular terrace widths. It is obvious that the CuCl islands grow without a discernible relation to the step edges of MgO(001), strongly suggesting the nucleation of CuCl on terraces of MgO(001), not on step edges. Further, it is striking that the CuCl islands have a highly concave top surface (Fig. 3(a)). The middle part of the island is thinner than the other parts, especially near the three particular sides perpendicular to [1$\bar{2}$1], [11$\bar{2}$] and [$\bar{2}$11]. This phenomenon is explained by a predominant surface migration of CuCl growing species from the substrate surface to the (111) top faces of the islands via particular side facets composed of CuCl{$\bar{1}\bar{1}\bar{1}$} and/or {110}.

In conclusion, we have shown that zincblende ionic compounds of CuCl and CuBr are grown epitaxially on MgO(001) with (111) growing surfaces and two different in-plane orientations of CuCl[1$\bar{1}$0] // MgO[110] and CuBr[1$\bar{1}$0] // MgO[100].

This results suggest that the interfacial matching in ionic configuration, i.e. in the distance between atomic rows of identical ions, is one of the keys in heterogeneous overlayer formation in ionic systems. The formation of relatively flat thin films of CuCl in a suitable growth condition has enabled us to observe the confinement effect of the center-of-mass motion of excitons in CuCl.[4]

References
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