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Epitaxial Insulating Fluoride Layers on Semiconductors

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IN HONOR OF SIR JOHN MEURIG THOMAS ON HIS 60TH BIRTHDAY

The epitaxial growth of the rare earth fluorides HoF_3 and GdF_3 on Ge, Si, and GaAs has been investigated. At the same time the detailed nature of the interfaces formed has been probed by X-ray photoelectron spectroscopy. Epitaxial layers can readily be grown and it is shown that layers with the high temperature tysonite-like phase may be prepared in such a way as to be stable at room temperature. A critical thickness exists where the layer structure changes to a multidomain orthorhombic form; this thickness is dependent on the degree of mismatch of the lattices of overlayer and substrate. Whereas the GdF_3–Ge interface is unreactive, strong reactions are seen for HoF_3–Si, GdF_3–GaAs, and LaF_3–Si. Reactions at the latter interface may be attenuated by an intermediate ordered layer of arsenic just one monolayer thick. © 1993 Academic Press, Inc.

Introduction

There exists significant interest in the possibility of fabricating device structures such as integrated circuits based on a three dimensional configuration. The fabrication of such structures would be facilitated by the availability of semiconductor–insulator–metal multilayer structures. This possibility has led to an interest in the growth of epitaxial single crystal insulating fluoride layers on semiconductors. Most investigations have concentrated on the alkaline earth difluorides or mixtures of them grown in a lattice matched form on Si and III–V semiconductor (*1*, *2*). These fluorides, however, have a rather large thermal mismatch (*3*) with most common semiconductors and are also slightly water soluble (*4*) which can be undesirable due to degradation of the layers in humid atmospheres.

The rare earth trifluorides, such as LaF_3, are not water soluble under normal conditions (*4*) and have a thermal expansion coefficient closer to those of the group IV and III–V semiconductors (*3*). LaF_3 has a trigonal, tysonite-like structure (*5*, *6*) at all temperatures and is in fact reasonably matched to InP. However, the rare earth trifluorides (REF_3) that might be more closely matched to Si, Ge, and GaAs possess an orthorhombic rather than a trigonal structure at normal temperatures (*7*), so that the question of epitaxy and lattice matching might at first appear irrelevant. However, closer inspection of these structures reveal that, over a narrow temperature range, solids such as HoF_3 and GdF_3 do in fact have a stable trigonal structure (*7*). This is shown in Fig. 1 where it may be seen that HoF_3 and GdF_3 appear to have stable tysonite structures above ~1000°C. Several interesting questions arise from this result, two of which will be addressed in this paper.

(i) Can layers of HoF_3 and GdF_3 be grown in such a way that the trigonal tysonite structure is retained, even to room temperature, by growth on an appropriate substrate?

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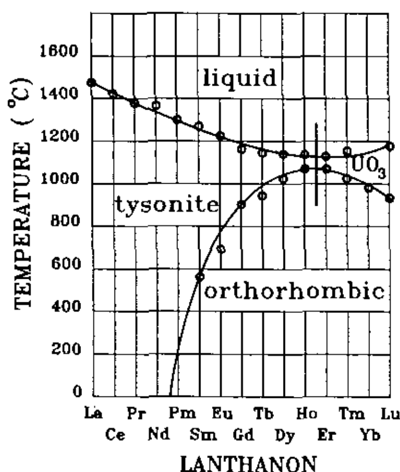

FIG. 1. Phase diagram showing the temperature dependent structural transitions for the REF_3s. Data taken from (7).

(ii) For systems which are not lattice matched, can strained layers be grown and does a "critical thickness" exist as observed in the strained layer growth of common semiconductors?

It will be seen that the answer to both questions is yes. Also presented in the following are results and discussion pertaining to the general nature of some of the interfaces formed. The systems we have chosen are HoF_3 on Si (111), where the lattaice mismatch with the trigonal structure is around 2%, as well as GdF_3 on Ge (mismatch 0.4%) and on GaAs (mismatch 0.4%). We briefly report also on the LaF_3–Si interface and in particular a method of reducing the interface reactions using an arsenic intermediate layer; abrupt and ordered interfaces are clearly desirable in any application.

Experimental

Layers of the REF_3 were deposited in ultra-high vacuum from a simple tungsten heated spiral, the deposited thicknesses being measured using a quartz crystal thickness monitor. The ordering of the layers was studied with LEED and the composition and interface reactions by X-ray photoelectron spectroscopy. Samples of Si and Ge were cleaned by heating to 1200 and 850°C respectively to produce (111) reconstructed surfaces, whereas GaAs (111)B clean surfaces were generated by heating arsenic capped MBE grown layers to drive away the cap.

Results and Discussion

(*a*) *Structure of the Fluoride Overlayers*

In general quite similar behavior was observed during the deposition of HoF_3 on Si(111), GdF_3 on Ge (111), and GdF_3 on GaAs (111) surfaces. This is illustrated in Fig. 2 by references to HoF_3 on Si (111). Here, HoF_3 was deposited on room temperature substrates which were subsequently annealed, or else the samples were maintained at elevated temperatures during fluoride deposition with all subsequent measurements being at room temperature. Figure 2 shows the LEED pattern after the deposition of 12 Å of HoF_3 at a substrate temperature of 750°C. This pattern is observed for HoF_3 thicknesses in the range 1–12 Å and resembles the Si $(\sqrt{3} \times \sqrt{3})R30°$ structure. For thickness of HoF_3 in excess of 12 Å the LEED pattern changes, giving that shown in Fig. 3c. The interpretation of these patterns is considered below and is much aided by the diagrams of the HoF_3 trigonal and orthorhombic structures shown in Fig. 4.

The HoF_3 layer with thickness in excess of 12 Å is in fact the orthorhombic structure. The (001) projection shown in Fig. 4b yields a rectangular surface mesh in reciprocal space (Fig. 3a) and it is clear that domains of this structure exist, such that each domain is rotated by 120° with respect to the others. The LEED pattern is synthesized from the three rotated rectangular arrangements as shown in Figure 3b. In particular the "three spot" arrangement readily identifies this three domain orthorhombic phase. The LEED pattern for thicknesses below 12 Å also reflects the HoF_3 structure but in this case it is the trigoinal "tysonite" structure, illustrated in Fig. 4a, that is observed. It is

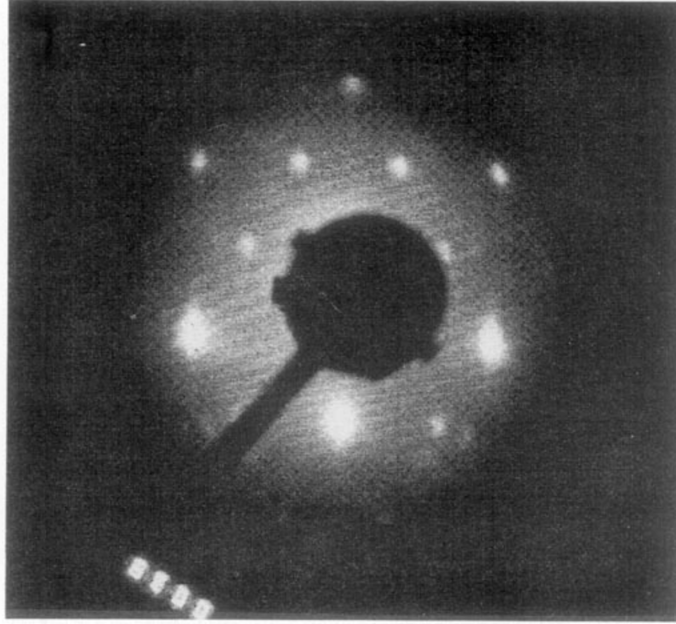

FIG. 2. LEED pattern recorded after ~12 Å of HoF_3 had been deposited onto atomically clean Si (111) at 750°C.

apparent that up to 12 Å the tysonite structure is indeed *stable at room temperature*. Beyond 12 Å the growth mode also changes from layer upon layer to an island growth mechanism. The 12 Å thus appears highly reminiscent of the critical thickness seen in the growth of strained layer semiconductors. The thickness is also of the order expected for a lattice mismatch of around 2%.

To further investigate the above possibilities similar experiments were carried out for trifluoride layers on Ge and GaAs. Here GdF_3 was chosen in view of its close match (0.4% to Ge and GaAs). Here again the trigonal structure was found to be stable at room temperatures for thin layers, up to around 180 Å for the Ge (111) substrates and 350 Å for GaAs. Beyond 200 Å the layers on Ge again display the multidomain orthorhombic structure. However, it is somewhat more complex than that for HoF_3 on Si and will be considered in detail elsewhere (*8*). The critical thickness is substantially greater for GdF_3 on Ge as expected. For GdF_3 on GaAs we have not so far observed the orthorhombic structure, but instead a disordered one, for thicknesses in excess of 350 Å.

(*b*) *Interface Reactions*

The precise chemistry of the fluoride–semiconductor interface was monitored by detailed X-ray photoelectron spectroscopy measurements as a function of thickness and annealing cycles. Figures 5 and 6 show previously published spectra (*9*) for HoF_3 on Si (111) for different temperatures and annealing times. Strong reactions are seen as evidenced by the large scale changes in the emission from the Si 2*p* core level. Detailed analysis shows that a holmium silicide is formed, with the associated loss of fluorine from the interface. The thickness of the silicide layer increases with annealing, and its metallic character leads inevitably to the pinning of the Fermi level at the interface. Exceptionally strong interface reactions were seen for GdF_3 on GaAs (111),

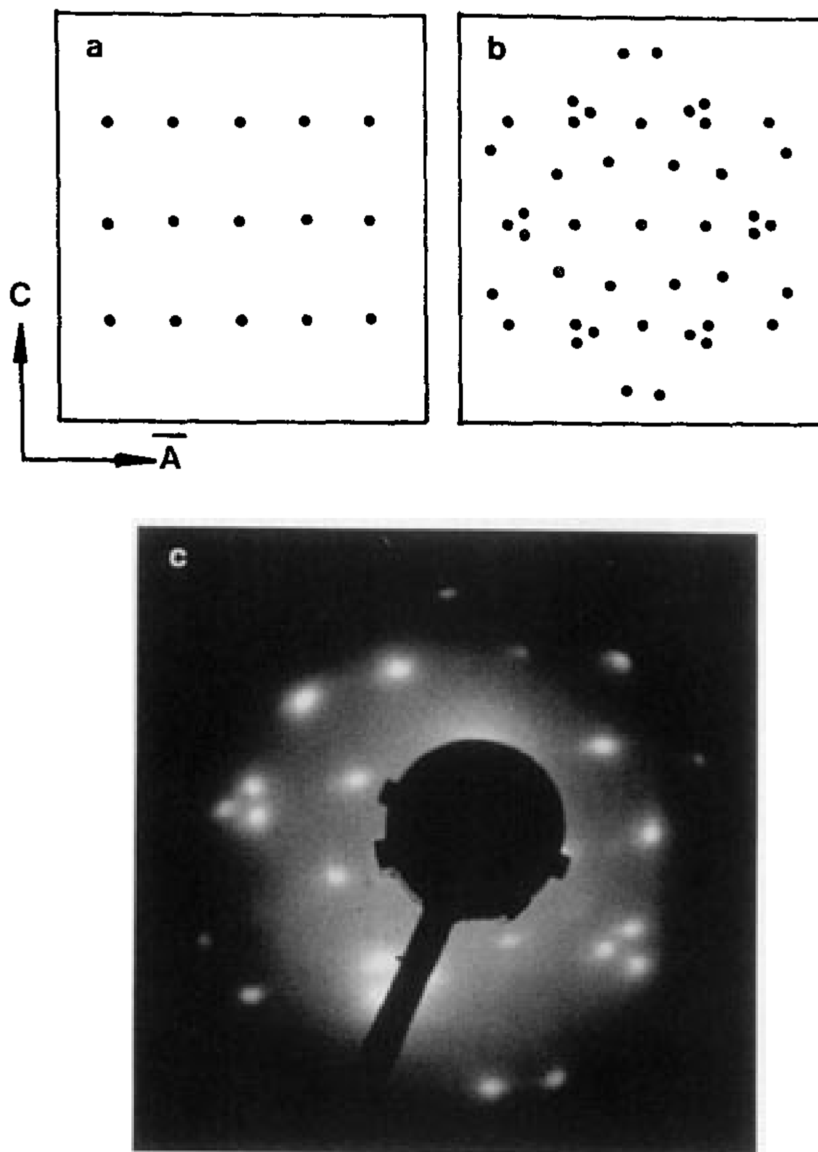

FIG. 3. (a) The reciprocal space mesh corresponding to orthorhombic HoF_3 in the [010] direction. (b) The mesh with an additional two components rotated by 120° and 240° respectively. This reproduces the LEED pattern shown in (c) which was recorded with an incident beam energy of 36 eV.

leading to a range of reaction products. For GdF_3 on Ge (111), however, we have so far not been able to detect the presence of interface reactions. Both of the above investigations will be described in full elsewhere (*8, 10*).

(*c*) *Reaction Barriers at Interfaces*

It is clear that the interface states associated with strong chemical reactions at the fluoride–Si and fluoride–GaAs interfaces are highly undesirable in any application. The suppression of reactions is thus an im-

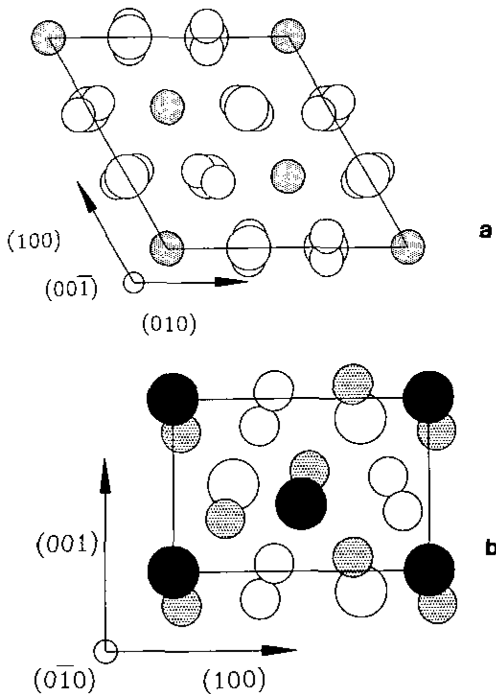

FIG. 4. (a) The unit cell of the orthorhombic structure of a REF_3 viewed along (010). The unit of cell of the triganal, tysonite-like structure of a REF_3 viewed along (001).

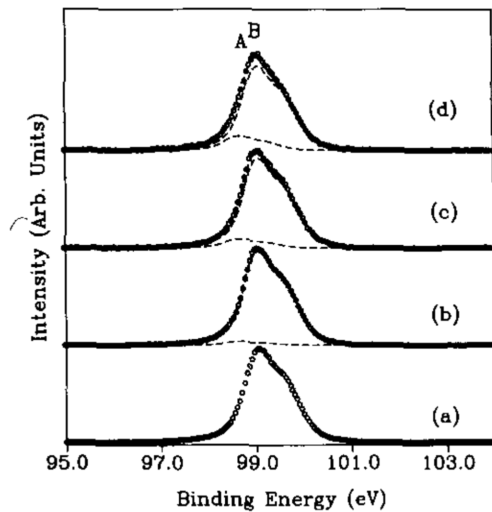

FIG. 5. Si 2*p* EDCs recorded (a) from the clean Si(111)-7 × 7 substrate and after (b)–(d) ~7 Å, 12 Å, and 41 Å respectively of HoF_3 had been deposited at a substrate temperature of ~700°C. Each spectrum has been scaled to the same height. Clearly, (b)–(d) can be synthesized with two components; B due to emission from bulk Si and A attributed to emission from Si bonded to Ho at the interface. A is offset from B by ~0.4 eV.

portant issue. To see how this may be aided we consider the case of LaF_3 on Si (111). In this case it is known that a lanthanum silicide layer is formed when the LaF_3–Si interface is annealed (*11*). This is apparent in the X-ray photoelectron spectra for LaF_3 on Si shown in the upper (c) and lower (a) parts of Fig. 7, where the La 4*d* doublet displayed a pronounced shift to lower binding energy associated with the silicide formation. The LaF_3 thick layer has the anticipated tysonite structure.

Figure 7 also shows spectra where the LaF_3–Si interface includes an arsenic interlayer (b). The As ordered monolayer was deposited on the Si (111) surface prior to the deposition of the LaF_3. It is clear that the form of the La 4*d* emissions changes very little upon annealing indicating significant suppression of the interface chemical reactions.

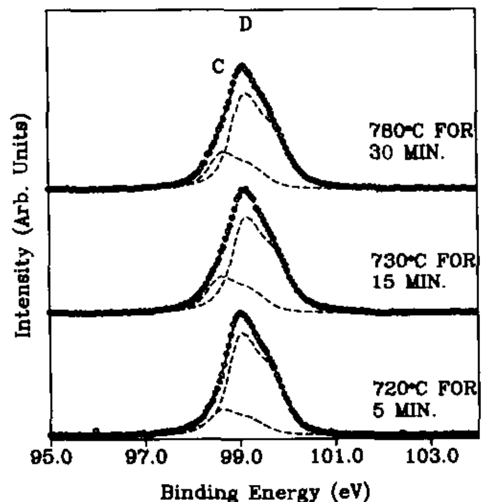

FIG. 6. Si 2*p* EDCs recorded as a function of annealing the 41 Å HoF_3 layer on Si mentioned in connection with Fig. 5. Each spectra can be synthesized with two components; C shifted by ~0.5 eV to the lower binding energy side of the bulk Si derived feature, D. Each spectrum has been scaled to the same height.

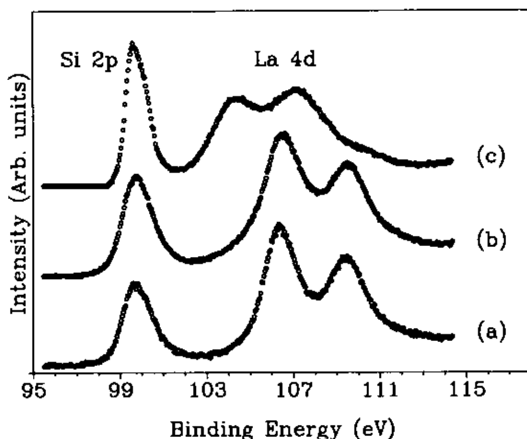

FIG. 7. (a) 10 Å of LaF_3 deposited onto Si (111) grown at RT. (b) 10 Å of LaF_3/As/Si (111) annealed at 500°C for 30 min. (c) 10 Å of LaF_3 on Si (111) annealed at 500°C for 30 min. Notice the large shift of the La 4*d* derived peak in (c) indicating the formation of a silicide. No reactions are evident in (a) or (b).

In conclusion we have shown that epitaxial insulating fluoride layers can readily be grown on group IV and III–V semiconductors. It is shown that structures normally stable only at high temperatures can be grown on Si and Ge such that the normally high temperature phase is stable at room temperature, thus considerably enhancing the range of suitable materials for epitaxial layers. The concept of a critical thickness, where the structures change from trigonal to orthorhombic is reminiscent of strained layers of group IV and III–V semiconductors. Interface reactions are common in the preparation of epitaxial layers and may lead to undesirable interface states. It is shown that chemical reactions can be substantially suppressed by the use of ordered monolayers deposited on the semiconductor before deposition and annealing of the fluoride layers. The potential of these findings is being further explored.

Acknowledgments

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