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Thin Solid Films 515 (2006) 448 – 451

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Crystalline structure of epitaxial $Ca_xMg_{1-x}F_2$ alloys on Si(100) and (111) substrates

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Abstract

Epitaxial growth of $Ca_xMg_{1-x}F_2$ alloy composed of cubic fluorite-type CaF_2 and tetragonal rutile-type MgF_2 on Si substrates was investigated as a possible method for fabricating lattice-matched ultra-thin dielectric layers. The crystalline structure of 1.2-nm-thick $Ca_xMg_{1-x}F_2$ alloy layers grown on Si(100) and Si(111) substrates by molecular beam epitaxy was characterized. On both Si(100) and Si(111), the grown $Ca_xMg_{1-x}F_2$ layers exhibited a cubic structure over a wide range of alloy composition ($0.2 \leq x \leq 0.9$). The surface was particularly smooth in the case of $x = 0.9$ on Si(111). It was found that, for both Si(100) and Si(111), the first two monolayers grown were composed of pure MgF_2 with a cubic structure. This is partly why the cubic $Ca_xMg_{1-x}F_2$ alloy was stable on the Si substrates.

PACS: 81.15.Hi; 61.66.Dk; 68.55.Jk

Keywords: Molecular beam epitaxy; Fluorides; Alloys; High energy electron diffraction

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1. Introduction

Heteroepitaxial structures composed of CaF_2 and CdF_2 grown by molecular beam epitaxy (MBE) on Si substrates are the most promising candidates for introducing quantum-effect devices into Si integrated circuits. CaF_2 and CdF_2 have a cubic fluorite-type structure, which is very similar to the cubic diamond-type structure of Si, and their lattice mismatches with Si at room temperature (RT) are +0.6% and −0.8%, respectively. The epitaxial $CaF_2/CdF_2/CaF_2$ heterostructures provide a deep quantum-well of 2.9 eV at the conduction band [1]. Utilizing these properties, resonant tunneling diodes (RTDs) operating at RT [2,3] have been fabricated on Si substrates and attempts have been made at integrating these with conventional Si devices [4]. However, these fluoride RTDs have insufficient stability and reproducibility so that it has not been possible to use them in circuit operation.

For stable and reproducible operation of fluoride RTDs, good quality heterostructures with abrupt interfaces without defects are required. The CaF_2 layer grown on Si presents problems as far as quality is concerned. These are related to the increase in lattice mismatch with the Si substrate at higher growth temperatures due to the greater thermal expansion of CaF_2 compared to that of Si. The lattice mismatch of CaF_2 with Si increases to +1.8% at the typical growth temperature of 750 °C from +0.6% at RT. The strain due to the lattice mismatch produces degraded structures such as pinholes and rough surfaces in the ultra-thin CaF_2 layers. It is thought that the formation of an alloy composed of CaF_2 and another fluoride material having a smaller lattice constant than Si would be effective in reducing the lattice mismatch.

Among fluoride materials with a cubic fluorite-type structure, only CdF_2 has a smaller lattice constant than Si. However, the $Ca_xCd_{1-x}F_2$ alloy layer is not suitable for growing directly on the Si surface because the CdF_2 molecular beam would react with the Si substrate [5,6]. By contrast, fluoride materials with a tetragonal rutile-type structure, namely MgF_2 and MnF_2, have a small lattice constant [7,8]. Especially, the reaction between MgF_2 and Si ($2MgF_2 + Si \rightarrow 2Mg + SiF_4\uparrow$) is not expected to occur because the Gibbs energy of formation has a large positive value of +568 kJ/mol. The lattice constants of MgF_2 at RT are $a = b = 0.462$ nm and $c = 0.305$ nm, which are much smaller than those of Si (0.543 nm) and CaF_2 (0.546 nm). Thus, it is expected that the lattice of the $Ca_xMg_{1-x}F_2$ alloy can be matched with that of the Si substrate. Indeed, it has been reported that X-ray diffraction of 70-nm-thick $Ca_xMg_{1-x}F_2$ alloy layers grown on Si(111) substrates coated with

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doi:10.1016/j.tsf.2005.12.254

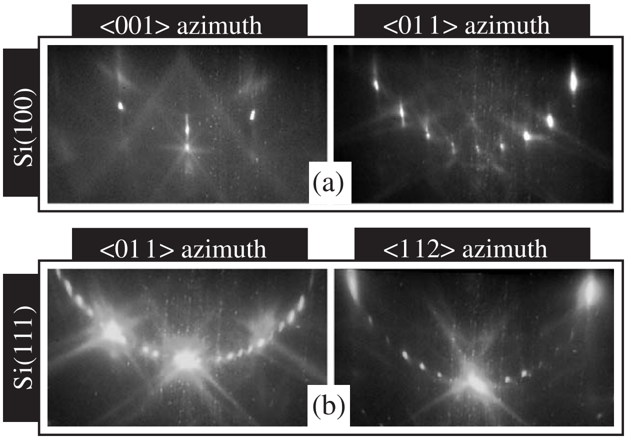

Fig. 1. RHEED patterns for thermally cleaned Si substrates: (a) Si(100) surface observed along the <001> and <011> azimuths; (b) Si(111) surface observed along the <011> and <112> azimuths.

CaF_2 buffer layers revealed the lattice match between a $Ca_{0.8}Mg_{0.2}F_2$ alloy and Si [7]. In view of the applications of $Ca_xMg_{1-x}F_2$ alloys to heterostructures composed of cubic fluorite-type crystals such as fluoride RTDs, the crystalline structure of $Ca_xMg_{1-x}F_2$ alloys composed of cubic CaF_2 and tetragonal MgF_2 should be determined. The present study characterizes the crystalline structure of ultra-thin $Ca_xMg_{1-x}F_2$ alloy layers grown directly on Si(100) and Si(111) substrates.

2. Experimental procedure

A solid-source MBE system, equipped with CaF_2 and MgF_2 K-cells and a reflection high-energy electron diffraction (RHEED) system, was used to grow fluoride layers on Si(100) and Si(111) substrates. Chemically cleaned Si substrates covered with a thin native oxide were loaded into the MBE chamber and heated at 900 °C for 20 min. These substrates exhibited super-periodic RHEED patterns reflecting surface reconstruction, as shown in Fig. 1. Thus, Si substrate surfaces can be cleaned in situ by this thermal method. The $Ca_xMg_{1-x}F_2$ alloy layers were grown by the simultaneous supply of CaF_2 and MgF_2 molecular beams to various thicknesses (several molecular layers (ML)) and compositions ($0 \le x \le 1.0$). The growth temperature was 350 °C, at which no reevaporation of these fluorides occurred. The alloy growth rates were adjusted to be around 0.8–1.0 nm/min. The crystalline structure of the $Ca_xMg_{1-x}F_2$ alloy layers on Si substrates was characterized in situ by RHEED patterns. The surface morphologies of the grown layers were observed by atomic force microscopy (AFM) of Nano Scope IIIa made by Digital Instruments Inc. The surfaces of all samples were observed with tapping mode in the air, immediately after the growth to avoid effects of exposure to the air.

3. Results and discussion

3.1. Crystalline structure of $Ca_xMg_{1-x}F2$ alloys on Si substrates

Fig. 2 shows the RHEED patterns of 1.2-nm-thick $Ca_xMg_{1-x}F_2$ layers grown on Si(100) substrates at 350 °C observed along the <001> and <011> azimuths of the Si(100) substrate. In the case of pure CaF_2 ($x = 1.0$) growth, symmetry patterns were obtained at these two azimuths, as shown in Fig. 2(a). These two patterns fit well the bulk spots of the cubic diamond structure of Si(100) shown in Fig. 1(a), indicating that the CaF_2 layer grown had a cubic fluorite structure. RHEED patterns exhibiting noncubic symmetry were obtained in the case of pure MgF_2 growth ($x = 0$), as shown in Fig. 2(b). These patterns were found to correspond to the MgF_2(112) surface of a tetragonal rutile-type structure. $Ca_{0.5}Mg_{0.5}F_2$ alloys grown on Si(100) substrates yielded diffraction spots at the same positions as those of pure CaF_2, as shown in Fig. 2(c). This cubic RHEED pattern was observed over a wide composition range ($0.2 \le x \le 0.9$). Thus, the $Ca_xMg_{1-x}F_2$ alloy layers were grown epitaxially with cubic fluorite structure on Si(100) substrates. A similar phenomenon was observed in the case of growth on Si(111) substrates, as shown in Fig. 3. The RHEED patterns of pure a CaF_2 layer showed a cubic fluorite-type structure, as shown in Fig. 3(a). Distinctly different patterns were observed in the case of growth of a pure MgF_2 layer, as shown in Fig. 3(b). These were found to correspond to the MgF_2(110) surface in a rutile-type structure. In the case of growth of $Ca_{0.5}Mg_{0.5}F_2$ alloys on Si(111) substrates, the RHEED patterns revealed cubic symmetry, as shown in Fig. 3(c). As in the case of growth on Si(100), this cubic pattern was observed over a wide composition range ($0.2 \le x \le 0.9$).

Sharp streaky RHEED patterns were observed in the case of growth of $Ca_xMg_{1-x}F_2$ alloy layers on Si(111) (see Fig. 3(c)), which corroborated surface smoothness. In particular, $Ca_{0.9}Mg_{0.1}F_2$ grown on Si(111) was found to yield the smoothest surface (Fig. 4(a)) across the entire composition range, including pure materials. This surface had a root-mean-square (RMS) value of roughness of 0.37 nm. For all compositions, RMS values of the grown surface were higher

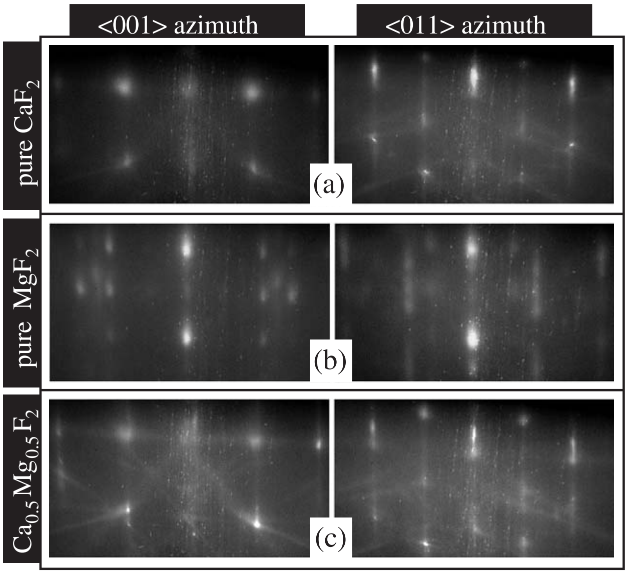

Fig. 2. RHEED patterns for 1.2-nm-thick $Ca_xMg_{1-x}F_2$ alloy layers grown on Si(100) substrates observed along the <001> and <011> azimuths of the substrate: (a) Pure CaF_2 ($x = 1.0$); (b) pure MgF_2 ($x = 0$) and (c) $Ca_{0.5}Mg_{0.5}F_2$ alloy.