

## CaF<sub>2</sub>/Si(111): Thin-film characterization by high-resolution electron-energy-loss spectroscopy

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High-resolution electron-energy-loss spectroscopy is used to investigate surface and interface phonons for thin epitaxial CaF<sub>2</sub> layers on Si(111). The dielectric approach used to describe the spectra is found to fail for ultrathin films. The spectra seem to show influences of strain in the film and of the crystalline quality at the interface.

CaF<sub>2</sub>/Si(111) and CaF<sub>2</sub>/Si(100) have attracted considerable interest<sup>1-8</sup> due to the close lattice match between CaF<sub>2</sub> and Si and its potential application in three-dimensional integrated-circuit technology. Studies have been performed on rather thick films (several hundred Å)<sup>1-8</sup> or very thin films (a few monolayers),<sup>9,10</sup> but rarely on film thicknesses interesting for future gate insulators (50–100 Å). Most analytical techniques applied to CaF<sub>2</sub>, like transmission electron microscopy or Auger electron spectroscopy<sup>11</sup> and to some degree even synchrotron-radiation spectroscopy<sup>12</sup> have been found to be destructive toward CaF<sub>2</sub> and have to be used with a great deal of caution. High-resolution electron-energy-loss spectroscopy (HREELS)<sup>13</sup> is usually regarded as a method limited to surface characterization. Only recently the first observation of interface phonons in a GaAs-Ga<sub>1-x</sub>Al<sub>x</sub>As superlattice has been reported.<sup>14</sup> In this Rapid Communication we present results for CaF<sub>2</sub>/Si(111) interfaces that clearly demonstrate the potential of the method to study properties of interfaces between a thin ionic, epitaxial overlayer and a semi-infinite substrate. HREELS probes the thin insulating film in a nondestructive way due to the low energy of the probing electrons (usually less energetic than the insulator band gap) and to the low current on the sample ( $< 10^{-12}$  A/cm<sup>2</sup>).

Cleaved high-purity CaF<sub>2</sub> single crystals as well as epitaxial layers on Si(111) surfaces were studied. *n*-type Si(111) wafers with a bulk resistivity of 10 Ω cm (phosphorous doped) were used. CaF<sub>2</sub>/Si(111) interfaces were prepared by molecular-beam-epitaxial (MBE) evaporation in an ultrahigh-vacuum (UHV) environment (10<sup>-7</sup> Pa during deposition). CaF<sub>2</sub> was deposited from a W crucible with a BN insert on heat-cleaned (850–900 °C, 60 sec) Si(111), kept at 700 °C during epitaxy. Different layer thicknesses between 10 and 5000 Å were produced.<sup>15</sup> The samples were transferred under inert atmosphere to another UHV system which held a HREEL spectrometer, type No. SEDRA (Riber, Inc.), with hemispherical monochromator and analyzer; they were heat cleaned before measurement. The spectrometer has been proven to have an ultimate resolution of about 3 meV.<sup>16</sup> For thicker insula-

tor layers and for the cleaved crystal the surface potential had to be stabilized<sup>17</sup> by irradiating the sample with the defocused beam of an electron gun (1 keV, 100–200 nA cm<sup>-2</sup>). No radiation damage could be detected in the vibrational spectra. The epitaxial samples showed surprisingly good-quality HREEL spectra, both with respect to angular distribution ( $\leq 1^\circ$ ) and with respect to reflected intensity compared to single-crystalline metal samples, indicating a high quality epitaxy. HREEL spectra of ionic materials recorded in a specular direction exhibit strong features related to the excitation of long-wavelength surface optical phonons, usually called Fuchs-Kliwer modes.<sup>18,19</sup> Their properties are mainly determined by bulk macroscopic optical parameters such as the frequency-dependent dielectric response. The dielectric theory<sup>20</sup> uses this response to describe the interaction of "fast" electrons with surface excitations. This theory is capable of quantitatively describing the HREEL spectra of ionic semiconducting and insulating single crystals<sup>16,21</sup> and derives infrared (ir) optical constants from HREELS data. These constants are generally found to match closely those derived from ir spectroscopy but are also found to reflect surface properties, e.g., surface states or roughness.<sup>21</sup>

A specular HREEL spectrum of a CaF<sub>2</sub> cleaved single crystal is shown in Fig. 1. It exhibits a single Fuchs-Kliwer surface phonon whose frequency can be determined accurately from the distance between successive multiple losses. The measured frequency of  $51.1 \pm 0.2$  meV agrees well with a calculation of the surface phonon frequency from the relation

$$\omega_{\text{FK}}^2 = \omega_{\text{TO}}^2 [\epsilon(0) + 1] / [\epsilon(\infty) + 1]$$

yielding  $51.05 \pm 0.1$  meV; where  $\omega_{\text{TO}} = 31.9$  meV is the frequency of the bulk transverse optical phonon,  $\epsilon(0) = 6.7$  and  $\epsilon(\infty) = 2.04$  are, respectively, the static and high-frequency dielectric constants<sup>22</sup> of CaF<sub>2</sub>.

Spectra of thin epitaxial CaF<sub>2</sub> films on Si(111) clearly exhibit the 51-meV surface optical phonon as well as an intermediate peak between the surface phonon and the elastic peak. As an example the spectrum of a 50-Å-thick

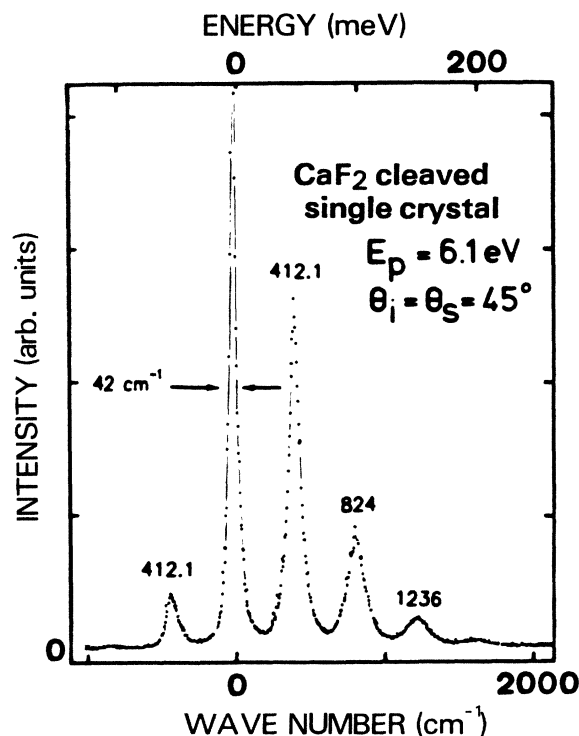


FIG. 1. Energy-loss spectrum of 6.1 eV electrons after reflection from a cleaved  $\text{CaF}_2(111)$  single crystal. The surface potential is stabilized by irradiation with electrons, 200 nA/cm<sup>2</sup> at 1 keV.

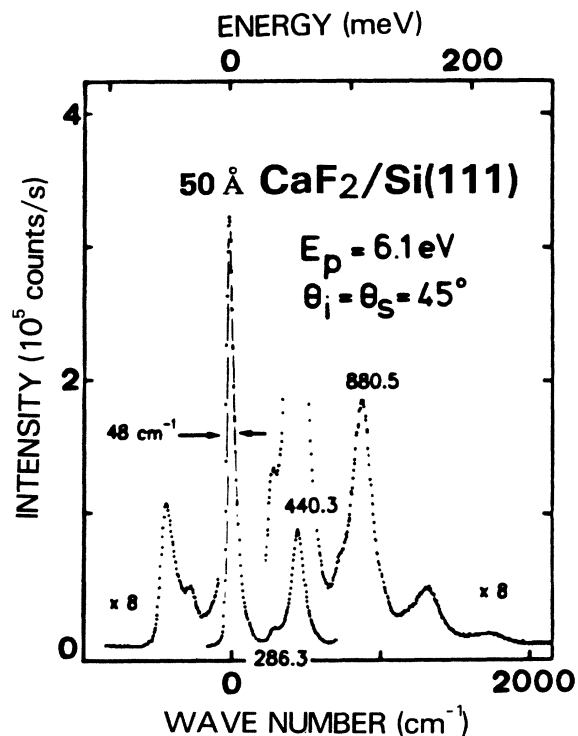


FIG. 2. Energy-loss spectrum of 6.1 eV electrons after reflection from a 50-Å-thick epitaxial  $\text{CaF}_2$  layer on  $\text{Si}(111)$ . No surface potential stabilization is needed under these conditions.

$\text{CaF}_2$  film on  $\text{Si}(111)$  is shown in Fig. 2. The energetic position of the intermediate peak is found to be dependent on the  $\text{CaF}_2$  layer thickness. To clearly identify the intermediate peak as an interface phonon its frequency has to be measured in spectra where the respective influences of surface and interface phonons are minimal on each other. The experimentally determined frequency for rather thick films ( $\sim 500$  Å) is compared with the frequency calculated for a phonon at the interface between  $\text{CaF}_2$  and an isotropic medium (Si) with dielectric constant  $\epsilon = 12$ . Solving the relation  $\omega_{FK}^2 = \omega_{FO}^2 [\epsilon(0) + 12] / [\epsilon(\infty) + 12]$  yields in this case  $36.9 \pm 0.1$  meV which agrees well with the experimental value of  $36.5 \pm 1$  meV. This latter value differs sufficiently from the Raman-active mode and the longitudinal or transverse optical mode energies for  $\text{CaF}_2$  of 40.0, 57.8, and 31.9 meV, respectively.<sup>23,24</sup> Moreover, excitations of Si-Ca or Si-F stretching vibrations at the interface can be ruled out as the weak nature of the chemical bond at the interface<sup>9</sup> gives rise to very low excitation cross sections.<sup>13</sup> Finally, attributing this 36-meV mode to another surface phonon can also be ruled out because the peak shows a very strong intensity dependence on layer thickness, becoming more intense for thinner layers. This allows us to unambiguously identify the intermediate peak as being the loss due to excitation of a phonon localized at the  $\text{CaF}_2/\text{Si}(111)$  interface.

The dielectric theory has recently<sup>25</sup> been expanded to describe arbitrarily layered structures. Its predictions were compared to the HREEL spectra of a  $\text{GaAs-Ga}_{1-x}\text{Al}_x\text{As}$  superlattice, and a good agreement was

found<sup>14</sup> for layer thicknesses as low as 100 Å. Because of the lack of strong chemical interaction and the consequently atomically abrupt interface<sup>26</sup> the  $\text{CaF}_2/\text{Si}$  system appears as a model system to compare theoretical predictions with experimental data. Indeed, frequency shifts of both the surface and the interface phonon with decreasing film thickness are predicted by the theory to occur in the thickness range around 100 Å.

The experimentally determined frequencies of both surface and interface phonons are plotted versus the film thickness in Fig. 3 (dash-dotted line) and compared to the theory<sup>27</sup> (solid line; the dashed region indicates vanishing phonon excitation cross section). It is clearly seen that the experimental data are in disagreement with predictions of the dielectric theory in two thickness regions. This theory is based on a classical electrodynamic description of the interaction process and can therefore be expected to fail for ultrathin films where quantum effects dominate. The disagreement for film thicknesses around 30–50 Å and below comes therefore as no surprise and a fully quantum-mechanical description<sup>28</sup> of the electron-phonon interaction process and the solid film seems necessary to accurately describe these data.

The disagreement between theoretical prediction and experiment in the thickness range up to about 1000 Å cannot be explained by an inadequacy of the theoretical approach in view of its success to describe superlattices;<sup>14</sup> it must be searched in the experiment. It has been found that, depending on the evaporation conditions, most of the lattice mismatch between  $\text{CaF}_2$  and Si (2.1%) during growth is taken up by misfit dislocations if the layer is

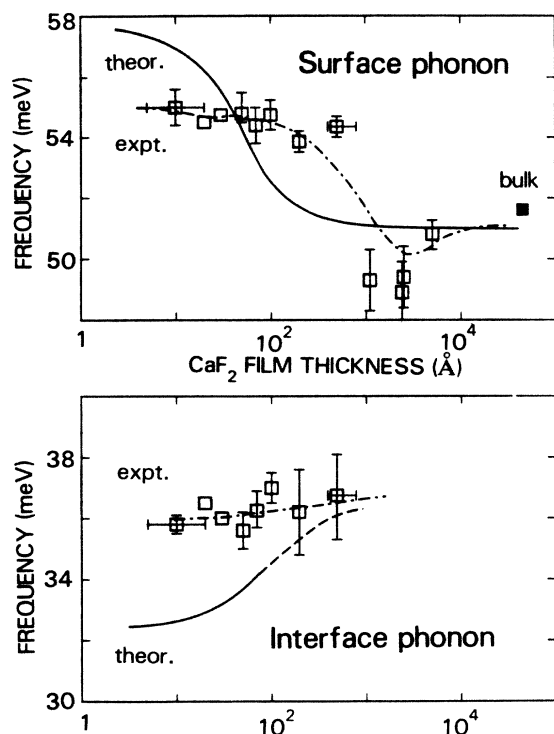


FIG. 3. Experimentally determined excitation energies of surface and interface Fuchs-Kliewer phonons for different epitaxial CaF<sub>2</sub> layer thicknesses on Si(111) substrates. The experimental data are connected by a spline curve (dash dotted). Results of calculation using the dielectric theory (Ref. 29) are shown as solid lines; the dashed part expresses vanishing excitation cross section.

thicker than about 300 Å.<sup>29</sup> The thickness range at which the surface phonon frequency is experimentally observed to change abruptly (Fig. 3) coincides with the thickness range for which misfit dislocations are formed and the CaF<sub>2</sub> film relaxes to its bulk lattice parameter. Changes in the lattice parameter modify the phonon frequencies of the lattice. Unfortunately, changes in the lattice parameter (i.e., different changes parallel versus perpendicular to the surface) correlate in no simple way to shifts of Fuchs-

Kliewer mode frequencies due to their elliptical polarization. Despite the present lack of a quantitative description, we conclude from the coincidence of the range of thicknesses for phonon-frequency shifts and lattice-parameter changes that HREELS is potentially capable of observing stress in epitaxial layers. Work is currently being performed to theoretically describe Fuchs-Kliewer phonons in strained lattices.

HREEL spectra of insulators are quantitatively described by using a fitting procedure based on the dielectric theory.<sup>16</sup> The fit permits determination of the transverse optical phonon frequency  $\omega_{TO}$ , the phonon oscillator strength  $\Delta\epsilon$ , and its damping  $\gamma$ . Phonon frequency and strength are generally found to agree with values determined by ir spectroscopy. Larger phonon dampings observed in HREELS compared to ir spectroscopy are attributed to mechanisms shortening the lifetime of phonons at the surface compared to bulk phonons, e.g., surface roughness.<sup>21</sup> For epitaxial CaF<sub>2</sub> layers on Si(111) we find as a general trend that the surface phonon is more strongly damped than the interface phonon. We conclude that the lifetime of the surface phonon must be shorter than that of the interface phonon. The HREEL spectra indicate no low-energy electronic excitations like surface states which might serve as possible channels for surface phonon deexcitation. This seems to indicate that the crystalline quality of the CaF<sub>2</sub>/Si(111) interface is better than that of the CaF<sub>2</sub> surface.

In conclusion, HREELS has been shown to probe interfaces at epitaxial insulator-semiconductor interfaces. Because of the low primary energy of the electrons the analysis of the surface and interface can be kept destruction free for thin layers. The method seems capable of detecting stress in epitaxial films as well as surface and interface quality. Limits of the dielectric theory often used to describe HREEL spectra are found to be in the quantum limit.

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