Sapphire surface polariton splitting due to resonance with aluminum nitride film phonon

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Abstract. Two thin aluminum nitride films have been prepared on sapphire substrates by molecular beam epitaxy technique. Then alkaline and acidic washing were used to remove the back-metal-coating of the sapphire substrate for one of the samples. (It caused also partial film dissolution). The surface polariton (SP) spectra have been measured by attenuated total reflection (ATR) technique. The measured SP dispersion is compared with one calculated using the literature film parameters. Due to the resonance interaction of sapphire substrate SP with the film transverse optical (TO) phonon the splitting of the dispersion curve of sapphire SP was found. The resonance takes place only for the frequency of the film TO phonon polarized along the surface of the anisotropic AlN film (perpendicular to the optical axis). The analysis of ATR and external reflectivity spectra shows the presence of some transition layer between the substrate and the film.

1. Introduction

Surface polariton (SP) is the excitation very sensitive to the state of the surface [1, 2]. It propagates along the interface between 2 media, if one of them is absorbing and exponentially decays out of the interface. For thin films or multilayer structures SPs on different interfaces interact resulting in SP shift and splitting. The splitting of SP at TO and LO film frequencies was predicted in [3] and experimentally observed in [4] for LO phonon of isotropic LiF films on various substrates including sapphire. The value of splitting depends on the film thickness and on the film excitation oscillator strength. These modes (as far as the single interface SP) are transverse magnetic (TM) SPs and can be excited in p-polarized light. If the resonance with film TO phonon takes place, a transverse electric (TE) mode (in s-polarized light) appears too (e.g. LiF film on CaF₂ [5]).

SP on the vacuum - aluminum nitride (AlN) interface has just been reported and discussed in [6, 7]. It exists almost in the same region as sapphire SP, and the TO frequencies of anisotropic AlN [8, 9] appear in the dispersion region of sapphire SP [1, 2]. So the resonance of sapphire substrate SP with TO phonon of AlN film can be expected. We have calculated SP dispersion for sapphire with AlN films solving equation (22) from [2]). The frequency dependences of the film and substrate dielectric functions were represented as a sum of high frequency dielectric constant $\varepsilon_\infty$ and a set of Lorentz oscillators (one oscillator for the film):

$$\varepsilon(\nu) = \varepsilon_\infty + \sum_{i} \frac{f_i^2}{(\nu_i^2 - \nu^2 - i\gamma_i \nu)}$$

where $\nu_i$ is the $i$-th vibrational mode frequency, $f_i$ is its oscillator strength, $\gamma_i$ is its width. The literature data for film [8, 9] and substrate [10] oscillator parameters were used. Solid curves
on the figure 1 show bare sapphire dispersion, SP dispersion curves on sapphire with 30 and 100 nm thick AlN films are shown by dash and dotted curves respectively. In the displayed region there are two SPs on the vacuum-sapphire interface. The film causes the splitting of the high-frequency SP at the film E vibrations TO frequency (669 cm\(^{-1}\)). This splitting increases with the film thickness. Note that similar splitting at the film A vibrations TO frequency (~610 cm\(^{-1}\)) does not appear. Numerical calculations of the ATR spectra for the structure under study using equation (23) from [2] show that the resonance takes place at the film E vibrations TO frequency and A vibrations LO frequency.

**Figure 1.** The calculated surface polariton dispersion for the AlN film on sapphire, using literature film and substrate parameters. Calculations were done for bare sapphire (solid curves) and for sapphire with 30 and 100 nm thick AlN films (dash and dotted curves). Horizontal lines show TO frequencies of AlN perpendicular to the surface (A) and along the surface (E). Optical axes of the film and the substrate are normal to the surface.

2. Sample preparation

Two wurtzite AlN epilayers were grown on metal-backed c plane sapphire substrates. The film growth has been performed in a Veeco Gen II molecular beam epitaxy system and using an EPI radio frequency plasma source to supply activated nitrogen with 7N purity. High purity aluminum (6N5) source was used in the Knudsen cell. Prior to AlN growth, 45 min nitridation of the sapphire substrates was performed at substrate temperature of 200\(^{\circ}\)C. The growth of AlN epilayers was done at substrate temperature of 900\(^{\circ}\)C. The crystalline quality of the AlN epilayers as revealed by XRD rocking curves measured at omega scan mode was about 17 minutes. The optical axis of the anisotropic AlN film is perpendicular to the surface.

Prior to the optical characterizations for one of the samples the back-metal-coating of the sapphire substrate was removed in the 1:20 NH\(_4\)OH:H\(_2\)O solution, followed by 1:50 HF:H\(_2\)O solution. Subsequently boiling aqua regia (3:1 HCl:HNO\(_3\)) was used. It was appeared that such cleaning procedure has strong effect on the AlN film partially solving it (see below).

3. Spectra measurements

The attenuated total reflection (ATR) measurements in Otto configuration [1] and the measurements of external reflectivity have been done using IFS66v (BRUKER) infrared Fourier-transform spectrometer. The ATR unit with KRS-5 prism (NPVO-1, LOMO) was used for various angles of incidence (20-60 degree in the prism) in p-polarized light to study transverse magnetic (TM) SP. The transverse electric (TE) modes were measured in s-polarized light. Grid polarizer on KRS-5 substrate was used. The spectral resolution was 2cm\(^{-1}\). The gap between the prism and the sample (varying from a few microns to dozens microns) was adjusted by mylar strips or by dust particles in the gap. The reflectivity unit (IPO-22, LOMO) was used for the external reflectivity spectra measurements at near normal incidence.

4. Results and discussion

The ATR p-polarized spectra for different angles of incidence in the prism are presented in figures 2 and 3. Angular dependence of the absorption bands in the spectra gives the dispersion of SP on the sample. It can be used for reconstruction of the film dielectric function.
The measured TM SP dispersion (squares on the figure 4) is compared with one calculated above. The splitting of the high-frequency sapphire SP at the film E vibrations TO frequency (669 cm\(^{-1}\)) is easy to see for the experimental points too. Quite big discrepancy in the high frequency region can be due to the presence of some transition layer at the film-substrate interface.

To understand the reason of so big discrepancy we have measured the external reflectivity s-polarized spectra of the samples at near normal incidence. They are presented in figure 5 by solid and dashed lines.

The main difference from the bare sapphire spectrum is the appearance of the sharp minima above 650 cm\(^{-1}\). Their origin is the presence of the TO phonons of the films polarized perpendicular to the optical axis [8] (E vibrations). Apart from that, a pronounced dip at ~890 cm\(^{-1}\) can be clearly seen. This frequency coincides with the LO phonon frequency of the film parallel to the optical axis [8] (A vibrations). On another hand the forbidden mode 889 cm\(^{-1}\) of sapphire was reported in [10]. It can start to be active if any transition layer exists near the film-substrate interface. The hypothesis of the transition layer presence seems to be most realistic. We could not fit the experimental reflectivity spectra supposing the presence only AlN film on sapphire. Only the introduction of the 100 nm thick transition layer allows that.
The dash-dotted and dotted lines in figure 5 show the best fit for AlN film thicknesses 400 nm (as prepared sample) and 40 nm (cleaned sample). Spectra fitting (dispersion analysis), varying both film and transition layer parameters, was done using SCOUT - SpectrosCopic Objects and UTilities, a WINDOWS application written by W. Theiß [11]. Fitting results are presented in the Table 1 together with the literature data. Note that for the films as high frequency dielectric constant, as longitudinal phonon frequency are lower than their bulk values and decreasing after back cleaning. It can be a result of the film porosity, increasing after sample washing.

Table 1. AlN phonon parameters. Literature [8, 9] data and spectra fitting results.

| Sample            | ε∞   | νTO, cm⁻¹ | νLO, cm⁻¹ | γ, cm⁻¹ | d, nm |
|-------------------|------|-----------|-----------|--------|-------|
| Bulk (E vibr.)    | 4.53 | 669       | 912       | 8      | >20000 |
| As prepared       | 3.4  | 662       | 768       | 12     | 400   |
| Back cleaned      | 2.46 | 670       | 762       | 9      | 40    |

The TE SP (like in [5]) has been observed for the sample under study in s-polarized ATR spectra just below the film TO phonon frequency.

5. Conclusions
Strong coupling of the sapphire substrate SP with the TO phonon of the AlN film splits the sapphire SP dispersion curve. Despite both dielectric functions of the media could influence on the SP TM mode, the splitting takes place only at the E vibrations frequency (along the film surface) rather then at the A vibrations frequency (perpendicular to the film surface). The transition layer is found between the film and the substrate. The back side cleaning causes strong solving of AlN film decreasing its thickness for one order of magnitude and increasing film porosity. Some results related to the back cleaned sample have been published in [12].

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