Optical confocal spectroscopy of SiC and AlN interfaces using Raman scattering and Optically Detected Magnetic Resonance

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Abstract. The thesis contains the investigation of transition layer between AlN and SiC and the investigation of AlN Raman peaks evolution with distance till interface. Moreover, ODMR spatial research of nonuniformly irradiated 4H-SiC was performed together with PL spatial spectroscopy.

1. Introduction
The investigation of interfaces between materials with different characteristics can illuminate the processes of an internal properties evolution. In conducted research several different objects are considered, namely, AlN grown on 6H-SiC and 4H-SiC nonuniformly irradiated by electrons.

In the first case, the interface between materials with high band gap difference is of great interest. This is due to the fact that the presence of different values of the band gap will lead to different spin and optical properties of spin centers. These centers can be located in AlN which is considered to be the host matrix for defects possessing optical spin polarization in the ground state. For example, in theoretical predictions [1] it was shown that lattice strain is an important factor in stabilizing the high spin state of a nitrogen vacancy in AlN. Also, the ODMR active defects were observed in AlN [2].

We study AlN grown on 6H-SiC and its transition layer, as well as the evolution of the combination peaks with the distance to the interface. The region of the presence of the crystalline phase of SiC and AlN is observed, which means the presence of a solid solution of these materials. Considering the huge difference in the band gap between SiC and AlN, this can lead to intermediate values of the band gap in a given region of the crystal. In this area, it is possible to observe and create ODMR active spin centers similar to the V2 centers in 4H-SiC, the investigation of which are also presented in this work.

2. Experimental setup
The Raman spectroscopy is a very prominent method of investigation of crystalline structure and polytype composition of solids. The advantage of this technique is also the possibility of undamaging control. This technique provided with a high-resolution spectrometer for a Raman peak identification. Continuous excitation photoluminescence (PL) spectroscopy can measure the reaction of the material to laser excitation. It is used e.g. for spin centers and quantum dots luminosity measurements.

Optically detected magnetic resonance (ODMR) is a powerful tool for the detection and analysis of paramagnetic centers in semiconductors. If it has the recombination possibilities, this method allows...
for obtaining information about the spin and charge state and paramagnetic centers concentration. Using ODMR, we can investigate and manipulate small amounts of paramagnetic centers up to one center [3].

2.1. Raman and PL setup

The experimental setup for Raman scattering and PL measurements consists of a laser with continuous excitation (\(\lambda = 532 \text{ nm}, P = 50 \text{ mW}\)) with a selective diffraction intensity filter, a set of four diffraction gratings with different characteristics, a confocal optical focusing scheme, an XYZ piezoelectric scanner and XYZ mechanical scanner.

2.2. ODMR setup

ODMR detection of V_{Si} in 4H-SiC can be conducted in several ways. Here we present the level anticrossing (LAC) detection scheme for V_{Si}. It consists of the electromagnet (0-20 mT) for sweeping through LAC magnetic field position, the excitation near infrared (NIR) laser (\(\lambda = 808 \text{ nm}, P = 600 \text{ mW}\)) exploiting the most efficient absorption near zero phonon line of V2 V_{Si} (1.352 eV, 917 nm), the NIR photodiode for V_{Si} PL detection and the lock-in amplifier with modulation coil for PL intensity change measurement which is ODMR contrast.

3. Experimental results

3.1. AlN/SiC raman spectroscopy

The investigations of AlN grown on 6H-SiC substrate were performed, using Raman spectroscopy. The investigation contains two branches: transition layer Raman measurements and Raman scattering in AlN depending on the distance to the AlN/SiC interface.

The AlN sample was grown on 6H-SiC substrate by physical vapor method namely sublimation sandwich method (SSM). The main growth temperature was 2000 °C, the distance between source and substrate was 3-10 mm, the temperature gradient was 5 °C/mm, the nitrogen pressure in the growth chamber was 0.3-1 atm. The SSM method is better described in [4].

Having the full width at half maximum (FWHM) parameter of confocal volume in \(yz\)-plane of sample about 1 mkm, we conducted research of Raman peak evolution with high precision. The results shown in figure 1 demonstrate the evolution of characteristic Raman peaks intensity of both SiC and AlN with the position of confocal volume across the interface. It evidences the existence of crystalline phase both of SiC and AlN meaning the existence of solid solution of these materials. Given the huge difference in band gap between 6H-SiC (\(E_g=3.05 \text{ eV}\)) and AlN (\(E_g=6 \text{ eV}\)), this can lead to intermediate values of the band gap in a given region of the crystal.

Also, the study of Raman peaks centre position and FWHM is performed. The results are presented in figure 2, it shows the evolution of two Raman peaks centre position and FWHM with distance till AlN/SiC interface. Geometry of Raman scattering experiment is the following: the \(c\) axis of 6H-SiC and AlN crystals is parallel to \(z\) axis, the interface plane is \(xy\)-plane, which is perpendicular to \(z\)-axis; linearly polarised laser beam propagates in \(x\)-direction, linear polarisation vector of laser is parallel to \(y\)-axis, Raman scattering is being detected in \(x\)-direction. The correspondent peaks are shown in figure 3. They are associated with \(A_{1}\) (TO) and \(E_{2}\) (high) phonon modes [5]. Since the thickness of AlN layer is about 1.1 mm, the results cannot be fully described accordingly with [6]. We observe the abrupt changes in both FWHM and position of Raman peaks around 0.6 mm distance to the interface and near the AlN surface, which can be connected with different circumstances such as growth conditions or local stress increase. We can see that peaks center positions change along with its FWHM parameters what indirectly confirms the last.
**Figure 1.** Integral Raman peaks intensity evolution with focus position in interface between AlN and 6H-SiC. The inset shows Raman spectra of AlN/SiC transition layer, the integration area is shown by a grey background.

**Figure 2.** Raman peaks center position and FWHM evolution with distance till interface in AlN grown on 6H-SiC.
3.2. ODMR and PL spectroscopy of 4H-SiC nonuniformly irradiated by electrons

The object in question is silicon vacancy (V_{Si}) in 4H-SiC. Currently, the model describing that spin centre assumes that silicon vacancy in SiC is being perturbed by carbon vacancy located along the crystalline axis c [7]. In 4H polytype of SiC there exist two inequivalent lattice sites for such a centres V2 and V1. These centres have PL in the NIR range (850-950 nm at room temperature).

The spin Hamiltonian of V_{Si} centre in the external magnetic field is the following:

\[ \hat{H} = g \mu_B B \cdot S + D \left( S_z^2 - \frac{1}{3} S(S + 1) \right), \]  

where the first and the second terms correspond to the Zeeman interaction and fine structure splitting, respectively, \( \mu_B \) is the Bohr magneton, \( g \) is electron g-factor, and \( S_z \) is the projection of the total spin on the symmetry axis of the centre.

The ground spin state of V_{Si} is \( S=3/2 \) and has zero field splitting parameter about 66 MHz. It has the unique ability to be optically aligned by nonresonant optical excitation leading to increasing of populations with \( m_S=\pm 1/2 \). Furthermore, the V_{Si} centre has strong photoluminescence dependence on the spin sublevels population in the ground state which can amount several per cent of PL change. Due to these features and the phenomenon of population equalisation in specific magnetic fields determined by LAC events we can perform ODMR spectroscopy [8].

The investigated sample of 4H-SiC was irradiated by the electron beam with flux density \( 2 \times 10^{18} \) cm\(^{-2} \), energy 2 MeV and diameter about 5 mm. Firstly, we conducted spatial PL measurements with laser excitation (\( \lambda=532 \) nm, P=50mW) that are presented in figure 4. We determined that PL intensity proportional to spin centre concentration is changing by 2.5 orders of magnitude from the centre of spot till the edge of crystal. Secondly, we obtain ODMR spectra for different points in crystal at the centre of the spot and at the edge of crystal; the insets in figure 4 and the full spectrum in figure 5 demonstrate that. The ODMR spectrum in figure 5 contains several resonance lines including two LAC signals which can be described by the energy level diagram in the inset in figure 5 and the hyperfine structure lines originating from the interaction with the second coordination sphere with a single Si^{29} atom.
4. Conclusion
The results presented in this paper have several significant points. The confocal Raman investigations of AlN grown on 6H-SiC substrate indirectly demonstrate the existence of solid solution phase on the interface between materials. The Raman peaks evolution in thick AlN layer reveals significant deviations of peaks centers and FWHM parameter behavior that we connect with local stress increase.
A solid solution of materials with such a difference in the band gap can be beneficial for changing the characteristics of spin centers implanted at the interface. Also, the Raman peaks behavior of AlN thick layer demands further investigations.

In the PL and ODMR research, we completely connected observed PL behavior with the $V_{Si}$ center concentration by observing appropriate resonance LAC lines in the ODMR spectra in the center of irradiation spot and in the edge of the sample.

References

[1] Seo H, Ma He, Govoni M and Galli G 2017 Designing defect-based qubit candidates in wide-gap binary semiconductors for solid-state quantum technologies Phys. Rev. Mat. 1 075002
[2] Soltamov V A et al. 2013 Shallow Donors and Deep-Level Color Centers in Bulk AlN Crystals: EPR, ENDOR, ODMR and Optical Studies Appl. Magn. Reson. 44 1139–65
[3] Christle D J, Falk A and Andrich P 2014 Isolated electron spins in silicon carbide with millisecond-coherence times Nat. Mater. 14(2) 160-63
[4] Mokhov E N and Wolfson A A 2018 Single Crystals of Electronic Materials. Growth and Properties ed R Fornary (Elsevier) pp 401-45
[5] Davydov V Yu, Kitaev Yu E, Goncharuk I N, Smirnov A N, Graul J, Semchinova O, Uffmann D, Smirnov M B, Mirgorodsky A P and Evarestov R A 1998 Phonon dispersion and Raman scattering in hexagonal GaN and AlN Phys. Rev. B 58(19) 12899
[6] Liu L, Liu B and Edgaret J H 2002 Raman characterization and stress analysis of AlN grown on SiC by sublimation J. Appl. Phys. 92(9) 5183
[7] Soltamov V A, Yavkin B V, Tolmachev D O, Babunts R A, Badalyan A G, Davydov V Yu, Mokhov E N, Proskuryakov I I, Orlinskii S B and Baranov P G 2015 Optically Addressable Silicon Vacancy-Related Spin Centers in Rhombic Silicon Carbide with High Breakdown Characteristics and ENDOR Evidence of Their Structure Phys. Rev. Lett. 115 247602
[8] Baranov P G, Bundakova A P, Soltamova A A, Orlinskii S B, Borovykh I V, Zondervan R, Verberk R and Schmidt J 2011 Silicon vacancy in SiC as a promising quantum system for single-defect and single-photon spectroscopy Phys. Rev. B 83 125203