Abstract: Ternary Ta$_2$NiSe$_5$ is a novel electronic material having the property of an excitonic insulator at room temperature. The electrical properties of Ta$_2$NiSe$_5$ have not been elucidated in detail. We discuss the electronic properties in Ta$_2$NiSe$_5$ films and the formation of heterojunctions. Hall effect measurements showed p-type conductivity. The activation energies estimated from the temperature dependence of the carrier concentration were seen to be 0.17 eV and 0.12 eV, at approximately 300 and 400 K, respectively. It was observed that carrier generation behavior changes at the critical temperature of the excitonic insulator state (328 K). The temperature dependence of the Hall mobility below the critical temperature nearly follows the bell-shaped curves for conventional semiconductor materials. A MoS$_2$/Ta$_2$NiSe$_5$ van der Waals heterojunction was fabricated using the transfer method. Rectification characteristics, which depend on the gate bias voltage, were obtained. The barrier height at the MoS$_2$/Ta$_2$NiSe$_5$ heterointerface and the on/off ratio could be modulated by applying a gate bias voltage, suggesting that the carrier transport was exhibited in band-to-band flow. Our demonstration suggests that the knowledge of Ta$_2$NiSe$_5$ increased as an electronic material, and diode performance was successfully achieved for the electronic device applications.

Keywords: Ta$_2$NiSe$_5$; electrical property; Hall effect measurement; heterojunction; diode

1. Introduction

Optoelectronic devices of layered materials offer several novel applications. In addition to electronic devices (field effect transistors [1] and memory devices [2]) and optical devices (light emitting devices [3] and photodetectors [4]), they have also been considered as metamaterials [5,6], which can be engineered to manipulate electromagnetic waves and to produce unconventional optical properties [7–9]. Transition metal chalcogenides have received much attention as novel optoelectronic materials. The physical properties of these materials are changed by the selection of constituent elements, such as semiconducting (MoW) (SSe)$_2$, superconducting FeSe$_2$ or NbSe$_2$, and ferromagnetic (CrFe)GeS$_3$ [10–13]. A layered structure is the most stable in many cases, and the film can easily be prepared by exfoliation and transfer from a single crystal. Therefore, in addition to applications that utilize unique properties, interface interactions caused by heterostructures with other materials have been investigated. In particular, ternary Ta$_2$NiSe$_5$ is a candidate for an excitonic insulator below the critical temperature of 328 K (Figure S1 in the Supplementary Materials) [14,15]. The analysis of energy band dispersion using angle-resolved photoemission spectroscopy indicated a flat valence band top [16]. In addition, conductivity and dielectric constant measurements have revealed the existence of excitons as distributed electric dipoles [17]. Furthermore, high-performance devices have been demonstrated as infrared photodetectors [18,19].

Here, we focused on Ta$_2$NiSe$_5$, for which the detailed electrical properties have not been elucidated, and there have been no demonstrations of heterojunctions with other materials. In the present study, we consider the growth of Ta$_2$NiSe$_5$ crystals by the vapor
transport method. The temperature dependence of the Hall effect was studied to investigate carrier dynamics such as activation and scattering. We have experimentally shown that the activation energy estimated from the temperature dependence of carrier concentration is different below and above the critical temperature of the excitonic insulator transition. In addition, a van der Waals heterojunction between Ta$_2$NiSe$_5$ and MoS$_2$ was fabricated, and diode performance was successfully achieved for the electronic device applications.

2. Materials and Methods

Ta$_2$NiSe$_5$ crystals were fabricated via the chemical vapor transport (CVT) method in sealed quartz tubes. Stoichiometric amounts of Ta plate, Ni chunk, and Se powder with a small amount of iodine (I$_2$) as a transport agent were placed in a quartz tube, which was pumped down below $5 \times 10^{-3}$ Pa from the open end using a rotary pump and a diffusion pump, after which the tube was sealed by high-temperature welding, as shown in Figure 1. The sealed quartz tube was placed inside an electrical furnace, and then heated at 900 °C for 1 week. Needle-shaped crystals were obtained at the low-temperature side end of the tube, which had a temperature that was approximately 10% lower than the source temperature due to the temperature gradient of the furnace.

![Figure 1. Schematic of the experimental setup for the preparation of Ta$_2$NiSe$_5$.](image)

The morphology and elemental analysis of the Ta$_2$NiSe$_5$ crystals were observed using scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (FlexSEM 1000, Hitachi High-Tech Corporation, Tokyo, Japan). Ta$_2$NiSe$_5$ crystals were characterized by microscopic Raman spectroscopy using the 532 nm line of a diode-pumped solid-state laser (LabRAM HR Evolution, HORIBA, Ltd., Tokyo, Japan). The temperature dependence of the Hall effect was probed, using the van der Pauw method, to characterize the transport properties. MoS$_2$/Ta$_2$NiSe$_5$ devices were fabricated using photolithography and lift-off processes. Electrode patterns were formed directly, and the electrodes were spin-coated with ultraviolet-sensitive positive-type resist, using microscope-based exposure equipment (Arms System Co. Ltd., Tokyo, Japan). Electrode metals of the Cr/Au stack were deposited via e-beam evaporation, without intentionally heating the substrate temperature.

3. Results

Figure 2a shows a typical crystal domain of the Ta$_2$NiSe$_5$ film with a rectangular form, and the corresponding elemental analysis. For the crystal structure of Ta$_2$NiSe$_5$, the monoclinic (C2/c) phase is the most stable. The crystal structure of Ta$_2$NiSe$_5$ is shown in Figure S1 in the Supplementary Materials. The top view of the unit cell corresponds to the (010) plane, which can be seen to have rectangular form. The film comprises Ta, Ni, and Se elements, and the ratio of EDX signals agreed with the stoichiometry of Ta$_2$NiSe$_5$. Figure S2 in the Supplementary Materials shows a whole spectrum of XPS analysis of the Ta$_2$NiSe$_5$ film, transferred onto the substrate. Several peaks of Ta, Ni, and Se were detected, along with C and O, from the residual polymer that was used for exfoliation. In addition, the narrow spectra of the Ta 4f, Ni 2p, and Se 3d signals are shown in Figure S2.
in the Supplementary Materials. The peak positions are ascribed to the Ta-Se and Ni-Se bonds of Ta₂NiSe₅ [16,19]. To determine the crystal structure of the Ta₂NiSe₅ film, room-temperature Raman spectroscopy was performed, as shown in Figure 2b. No impurity peak was observed at approximately 106 cm⁻¹. Predominant peaks at 97.2 and 122.1 cm⁻¹, corresponding to A_g¹ and A_g² symmetry vibrations, and small peaks at 147.1, 176.4, 190.2, 213.8, and 288.0 cm⁻¹, corresponding to A_g³, A_g⁴, A_g⁵, A_g⁶ and A_g⁸, were observed. In particular, A_g¹ and A_g² can be confirmed as the monoclinic phase, which is identified as an excitonic insulator [20,21].

Figure 2. (a) SEM image of the Ta₂NiSe₅ film with elemental analysis of EDX; (b) Raman spectrum of the Ta₂NiSe₅ film.

Figure 3a,b shows the temperature dependences of the carrier concentration and carrier mobility, respectively. The temperature range is between 25 and 400 K, where p-type conductivity was observed, as described in previous studies [19]. Furthermore, as shown in Figure S3 in the Supplementary Materials, the transfer characteristics of the back-gate device exhibit p-type conductivity as well. The carrier concentration increased by more than five orders of magnitude with the increase in temperature, implying typical hopping conduction. However, no thickness dependence of the carrier concentration was observed. The activation energy E₀ was approximately 0.17 eV, estimated at approximately 300 K, which is a significantly deep energy position. Although Ta₂NiSe₅ is a zero-gap semiconductor (E_g < 50 meV) without an excitonic insulator phase, the opening of an excitation gap leads to an apparent energy bandgap of 0.36 eV due to the formation of the electron-hole bound state (the excitonic insulator phase) [22]. Therefore, the effective mobility edge of the hole flattens the valence band below the critical temperature T_c of the excitonic insulator transition (328 K), as shown in Figure S1 in the Supplementary Materials. The activation energy indicates the supply of holes contributing to the electrical conduction from the valence band to the new excitation state, which is similar to the hopping conduction of a typical semiconductor.

In contrast, the E₀ at approximately 400 K was also estimated to be approximately 0.12 eV, which is smaller than that below T_c. The apparent energy bandgap was decreased by excitonic fluctuations due to the unstable binding state. The temperature dependence of the carrier concentration was confirmed in the excitonic state. Furthermore, Hall mobility as a function of temperature followed a typical bell-shaped curve, which is restricted by phonon scattering at approximately room temperature (proportional to T⁻¹.5) and by ionized impurity-scattering at low temperature (proportional to T¹.5), similar to the observations in classical semiconductors. Above T_c, hole mobility was not dependent on temperature. In addition, in the low-temperature region, the exponent was slightly small (T¹.1), indicating that the two scattering mechanisms were mixed [23]. These results indicate that the electrical characterizations of the Ta₂NiSe₅ film below T_c of the excitonic insulator transition could be understood as similar to those of conventional semiconductors.
Figure 3. Temperature dependence of (a) carrier concentration and (b) Hall mobility for different thicknesses of Ta$_2$NiSe$_5$ films. The inset of (a) presents an enlarged view of the data near the $T_c$ (328 K, 3.05 K$^{-1}$) of the excitonic insulator transition.

The van der Waals heterojunctions of Ta$_2$NiSe$_5$ with other layered materials were investigated. An unintentionally doped n-type MoS$_2$ film was transferred onto a Ta$_2$NiSe$_5$ film on a SiO$_2$/Si substrate using a polymer sheet [24]. Figure 4a shows the current density-voltage ($J$-$V$) characteristics of the MoS$_2$/Ta$_2$NiSe$_5$ heterojunctions, where bias voltage was applied to the Ta$_2$NiSe$_5$ contact with respect to the MoS$_2$ contact. A back-gate bias was also applied. The inset of Figure 4a shows optical microscopy images of the MoS$_2$/Ta$_2$NiSe$_5$ heterojunction, where the device is assumed to have a junction area of 330 $\times$ 10$^{-8}$ cm$^2$. A diode-like rectifying behavior with a turn-on voltage of approximately 0.4 V was achieved. The current density depended on the gate bias voltage, indicating modulation of the barrier height. Figure 4b shows the gate bias voltage dependence of the barrier height at the MoS$_2$/Ta$_2$NiSe$_5$ heterointerface, which was estimated using the Richardson-Dushman equation,

$$J = A^* T^2 \exp \left( \frac{q \Phi_B}{k_B T} \right) \left[ \exp \left( -\frac{qV}{nk_B T} \right) - 1 \right]$$

(1)

where $J$ is the current density, $A^* = 4\pi m^* k^2 / h^3$ is the effective Richardson constant, $m^*$ is the hole effective mass, $h$ is the Planck constant, $\Phi_B$ is the barrier height, $n$ is the empirical ideality factor, and $V$ is the applied bias voltage. Figure 4c shows that the rectification (on/off) ratio depends on the gate bias voltage, defined as the ratio of the forward/reverse current density. The barrier height decreased slightly as the gate bias increased. The gate bias voltage corresponding to the maximum on/off ratio was $-5$ V. This is because the band alignment is modulated by tuning the Fermi level [25]. In our results, the carrier transport contributing to the current was exhibited in the band-to-band flow. In the case of an incomplete heterojunction, the $J$-$V$ characteristic had a relatively high turn-on voltage, as shown in Figure S4 in the Supplementary Materials, owing to tunneling transport through a relatively large van der Waals gap [26]. Compared to the heterojunction with the complete interface, the current density decreased in all voltage ranges, and the on/off ratio remained unchanged. The tunneling transport of heterojunctions can be stably controlled by inserting hexagonal boron nitride as a thin insulator at the interface [27], and is expected to exhibit high device performance (Figure S5 in the Supplementary Materials).
Supplementary Materials: The following materials are available online at https://www.mdpi.com/article/10.3390/coatings11121485/s1: Figure S1: crystal structure and band diagram of layered Ta$_2$NiSe$_5$; Figure S2: the chemical bond state characterized by X-ray photoelectron spectroscopy (PHI Quantera II$^\text{TM}$, ULVAC-PHI Inc.); Figure S3: transfer characteristic of back-gate Ta$_2$NiSe$_5$ field-effect device; Figure S4: current density-voltage ($J-V$) curve of the MoS$_2$/Ta$_2$NiSe$_5$ heterojunction with incomplete interface; Figure S5: $J-V$ curve of the MoS$_2$/h-BN/Ta$_2$NiSe$_5$ heterojunction with incomplete interface.

Author Contributions: Conceptualization, N.U. and Y.H.; methodology, M.F. and N.U.; validation, M.F., N.U. and Y.H.; formal analysis, M.F. and N.U.; investigation, M.F. and N.U.; resources, N.U.; data curation, M.F. and N.U.; writing—original draft preparation, N.U.; writing—review and editing, N.U. and Y.H.; supervision, Y.H.; project administration, N.U. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Figure 4. (a) $J-V$ characteristics of the MoS$_2$/Ta$_2$NiSe$_5$ heterojunction depending on gate bias voltage; (b) barrier height at the MoS$_2$/Ta$_2$NiSe$_5$ heterointerface; and (c) rectification ratio depending on gate bias voltage.

4. Conclusions

The electronic properties and formation of heterojunction devices for Ta$_2$NiSe$_5$ films were investigated. The majority carriers were holes, as determined by the Hall effect measurement. The activation energy estimated from the temperature dependence of the carrier concentration was 0.17 eV at approximately 300 K, which is close to half of the apparent energy bandgap of the excitonic insulator state. In addition, the activation energy was 0.12 eV at approximately 400 K, indicating an unstable exciton state due to thermal fluctuation. The temperature dependence of Hall mobility below the critical temperature of an excitonic insulator nearly follows the usual temperature dependence observed in conventional semiconductor materials. The van der Waals heterojunction of the MoS$_2$/Ta$_2$NiSe$_5$ structure was demonstrated. Diode-like $J-V$ characteristics, depending on the gate bias voltage, were achieved. The barrier height at the MoS$_2$/Ta$_2$NiSe$_5$ heterointerface and the on/off ratio were modulated by applying a gate bias voltage, suggesting that the carrier transport was exhibited in band-to-band flow. Our demonstration suggests that the knowledge of Ta$_2$NiSe$_5$ increased as an electronic material, and diode performance was successfully achieved for the electronic device applications.
Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: A part of this work was carried out using the analysis facilities at the Global Aqua Innovation Center (AICS) at Shinshu University.

Conflicts of Interest: The authors declare no conflict of interest.

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