

Charge Transfer in 1T-TaS₂/Graphene Hybrid Structures Studied by Spatially Resolved Raman Spectroscopy

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Graphene/1T-TaS₂ hybrid structures were measured using the Raman spectroscopy at room temperature. Spatially resolved Raman maps show that the region for which an effective graphene *G* band shift was observed correlates well with the tantalum disulfide flake, suggesting a change of the carrier concentration in graphene induced by 1T-TaS₂. This effect was observed only for the sample exfoliated in vacuum, which signifies the necessity of preventing tantalum disulfide from oxidation during sample preparation.

topics: Raman scattering, graphene, 1T-TaS₂, hybrid structures

1. Introduction

Tantalum disulfide (TaS₂) belongs to the family of layered transition metal dichalcogenides (TMDs). The 1T polytype (1T-TaS₂) is characterized by four successive temperature-dependent phase transitions associated with charge density wave (CDW) phases and structural changes of the crystal lattice. At high temperatures the material is metallic, whereas at low temperatures (below around 200 K) periodic lattice distortion occurs, leading to superlattice formation and a bandgap opening [1]. Moreover, 1T-TaS₂ has a relatively high value of spin-orbit interaction [2]. The possibility of piling up layers of different two-dimensional materials into so-called hybrid structures showing new properties started a new trend in semiconductors science, referred to as “nano-lego” [3]. The aim of the presented research is to obtain 1T-TaS₂ and graphene hybrid structures in order to combine the astonishing properties of these two materials, especially to obtain hybrid structures with strong spin-orbit coupling induced in graphene.

2. Methods

For the first approach, the investigated 1T-TaS₂/graphene structures were obtained by mechanical exfoliation of a 1T-TaS₂ crystal under ambient conditions onto epitaxial graphene grown on a silicon

carbide substrate (4H-SiC). The TaS₂/graphene interface was successfully excited through the transparent 4H-SiC substrate. However, accessing the TaS₂/graphene interface through the substrate resulted in reduced visibility and, therefore, only thick bulk TaS₂ flakes were detected and examined. The second type of samples was obtained by mechanical exfoliation in vacuum of TaS₂ flakes onto epitaxial graphene grown on a SiC substrate. Such a procedure prevented TaS₂ flakes from oxidation in ambient conditions. This sample was directly excited through semi-transparent thin 1T-TaS₂ flakes.

The samples were examined by means of the Raman spectroscopy, using a Renishaw InVia spectrometer. A continuous wave Nd:YAG laser operating at 532 nm was used as an excitation source. The laser light was focused on the sample using a $\times 100$ microscope objective yielding an excitation spot diameter of about 1 μm . The excitation power was kept low enough to prevent destruction of the investigated structures. Spatial Raman scattering maps were obtained using a precise *x-y* stage, operating with a spatial resolution of about 0.1 μm . All measurements were performed at room temperature.

3. Results

The Raman spectra of 1T-TaS₂/graphene hybrid structures obtained in air, excited through a SiC substrate are presented in Fig. 1. They

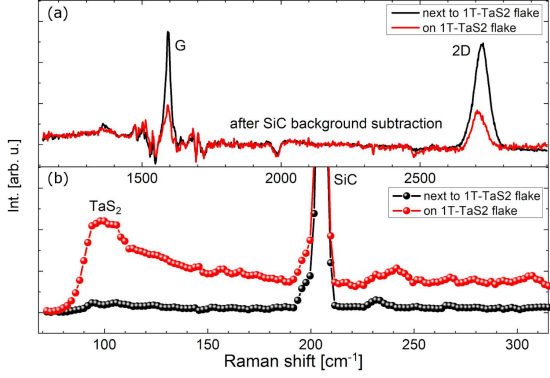


Fig. 1. Raman scattering spectra of 1T-TaS₂/graphene hybrid structure, prepared in air, measured through the SiC substrate on and next to a 1T-TaS₂ bulk flake in (a) the graphene bands energy range (after SiC background subtraction) and (b) 1T-TaS₂ energy range.

clearly comprise components from 1T-TaS₂ as well as from graphene and the 4H-SiC substrate. After careful subtraction of the SiC Raman spectrum in the energy range of 1000–3000 cm⁻¹, signals from 1T-TaS₂ and graphene can be analysed as presented in Fig. 1. Evidently, the observation of narrow G and 2D bands together with the absence of a D peak proves the high quality of graphene [4] (see Fig. 1a). Note that we observed some distribution of G and 2D band positions in our samples originating from graphene’s terraces, which is evident after careful inspection of Fig. 2. The broad band observed around 100 cm⁻¹ in Fig. 1b corresponding to 1T-TaS₂ Raman scattering is in good agreement with literature room temperature spectra [5]. However, its shape is significantly modified by attenuation caused by the edge Raman filter.

Results of the analysis performed on the data obtained from a linear Raman map of a typical

1T-TaS₂ crystal placed onto graphene are shown in Fig. 2. Interestingly, a considerable decrease of the intensity of the G and 2D peaks correlates well with the integrated intensity of the TaS₂ Raman signal, which clearly indicates that an interaction between graphene and the 1T-TaS₂ flake is present. However, no evident modification of the positions or widths of the G and 2D modes caused by the presence of the 1T-TaS₂ flake was observed. These results suggest that no significant charge transfer between 1T-TaS₂ and graphene takes place and that the effect most probably results from an excitation transfer between graphene and 1T-TaS₂. The observed oscillation of the parameter values related to the graphene lines can be connected with the step bunching of the SiC substrate [6].

Now we will concentrate on samples characterized by a clean interface. Spatially resolved Raman scattering maps of 1T-TaS₂/graphene hybrid structures obtained using high-vacuum exfoliation are shown in Fig. 3. Maps 3a and 3b present the Raman shifts of G and 2D band, respectively. In order to estimate the carrier concentration in graphene induced by the interaction with 1T-TaS₂, the effect of strain on G line energy was subtracted accordingly

$$\Delta E = E_G - E_G^0 - f(E_{2D} - E_{2D}^0), \quad (1)$$

where E_G is the G band energy, while E_{2D} is the 2D band energy. Here, we select $f = 0.3$, based on an analysis similar to [7]. Importantly, $E_G^0 = 1580$ cm⁻¹ ($E_{2D}^0 = 2680$ cm⁻¹) corresponds to the position of the G (2D) band for undoped, freestanding graphene [4, 7]. The observed effective G-band shift (Fig. 3d) caused by free carrier concentration [8] shows an evident spatial correlation with the Raman signal corresponding to 1T-TaS₂ (see Fig. 3c). This indicates a change of the carrier concentration in graphene induced by the 1T-TaS₂ flake. The induced concentration can be estimated to be in the range of 10¹²–10¹³ cm⁻². This result emphasizes the importance of preparation of 1T-TaS₂ structures in vacuum.

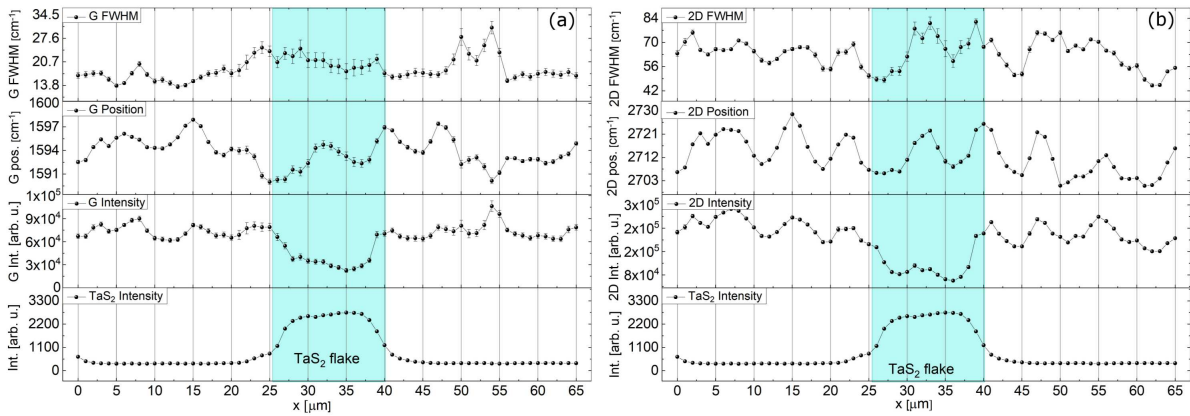


Fig. 2. Graphene Raman (a) G and (b) 2D band parameters including energy positions, full widths at half maximum (FWHM) and intensities obtained for graphene on (blue shadow) and next to 1T-TaS₂ crystal for the structure prepared in air.

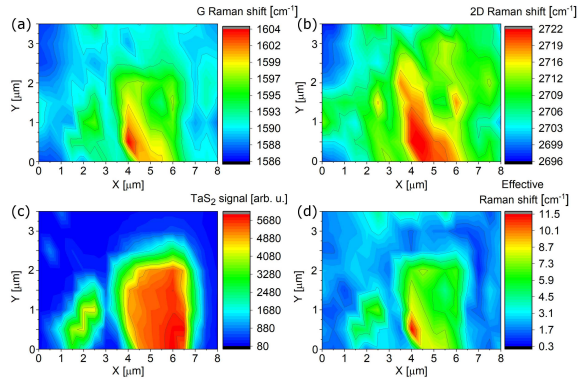


Fig. 3. Spatially resolved maps covering the area of $8 \mu\text{m} \times 3.5 \mu\text{m}$ of (a) G band Raman shift, (b) $2D$ band Raman shift, (c) Raman signal from $1T\text{-TaS}_2$ flake, (d) effective G band Raman shift (see (1)) measured on and next to a $1T\text{-TaS}_2$ flake, for the structure prepared in vacuum.

4. Conclusions

Room temperature Raman scattering measurements performed on the $1T\text{-TaS}_2/\text{graphene}$ hybrid structures obtained by high-vacuum exfoliation show an interaction between these two materials. Importantly, graphene's effective G band shift suggests a charge transfer between $1T\text{-TaS}_2$ in its metallic phase and graphene. However, no change of carrier concentration was observed for samples prepared in air, which stresses the necessity of preserving $1T\text{-TaS}_2$ flakes from contact with oxygen during preparation. Further studies are required in order to examine the interaction between tantalum disulfide and graphene at low temperatures, for the insulating phase of $1T\text{-TaS}_2$.

Acknowledgments

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