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Nitrogen acceptor in 2H-polytype synthetic MoS₂ assessed by multifrequency electron spin resonance

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Electron spin resonance (ESR) study on 2H-polytype synthetic MoS₂ revealed the N acceptor dopants as being characterized by a spectrum of axial symmetry [$g_{\parallel} = 2.032(2)$; $g_{\perp} = 2.270(2)$], typical for a hole-type center in MoS₂. The N impurities substitute for S sites, with a density of $\sim 2.3 \times 10^{17} \text{ cm}^{-3}$, which accounts for the overall p-type doping. With respect to measurements for the applied magnetic field directed along the *c*-axis, the signal consists of a ¹⁴N primary hyperfine triplet of splitting constant $A_{\parallel} = 14.7 \pm 0.2 \text{ G}$ superimposed on a correlated Gaussian single central line of peak-to-peak width $\Delta B_{pp} = 15.3 \pm 0.5 \text{ G}$, the latter making up only $\sim 26\%$ of the total signal intensity. The current work extends on these results through extensive monitoring of the temperature (*T*) dependence of salient ESR parameters and studying the impact of thermal treatment. ESR signal saturation studies indicate a N acceptor spin–lattice relaxation time T_1 (4.2 K) $\approx 3 \times 10^{-4} \text{ s}$, notably different from the much smaller As acceptor's T_1 in geological MoS₂. Concerning the thermal stability of the dopant, the N acceptor is found to be drastically passivated when exposed to H₂ at $\sim 500^\circ\text{C}$. Yet, subsequent reactivation attempts in vacuum at temperatures up to 740°C appear unsuccessful, urging great caution with conventional forming gas treatments at $T \gtrsim 500^\circ\text{C}$. Combination of careful K- and Q-band ESR monitoring of the *T*-dependent signal intensity resulted in the consolidation of the N dopant as a shallow acceptor of activation energy $E_a = 45 \pm 7 \text{ meV}$. The consolidated results establish N as a promising candidate for stable covalently bonded p-type doping of MoS₂ layers intended for application in novel nanoelectronic devices. *Published by the AVS.* <https://doi.org/10.1116/1.5034447>

I. INTRODUCTION

Two-dimensional (2D) nanomaterials have arisen as increasingly appealing for pushing the boundaries of current semiconductor technology due to compelling features like the emergence of new physical properties in the transition from bulk to 2D materials and the promising potential to create a multitude of innovative device structures.^{1–6} Among the 2D materials, layered transition metal dichalcogenides (TMDs) experience an ever-growing research interest as these could potentially replace traditional semiconductors in next generation nanoelectronic devices.^{1–3,5–7}

Among the extensive group of TMDs, molybdenite (MoS₂) has raised particular research interest: it is a strong, flexible, and atomically thin 2D layered semiconductor with a direct bandgap of $\sim 1.85 \text{ eV}$ in covalently bonded S-Mo-S monolayer form and an indirect bandgap of $\sim 1.3 \text{ eV}$ in bulk form.^{1,2} Moreover, due to the interlayer van der Waals bonding nature of TMD sheets, multimaterial stacking without lattice mismatch issues is made possible, hence enabling the combination of different optical, mechanical, and electrical properties to potentially create innovative devices with augmented functionality.⁸ The unique material properties of TMDs, and MoS₂ in particular, make them remarkably suitable for application in integrated circuits and optoelectronic devices, like solar cells, and flexible and transparent electronics.^{1,2}

Obviously, full exploitation of the outstanding properties of thin MoS₂ layers in novel TMD-based devices, including bipolar structures, will require the ability to properly control doping characteristics like dopant concentration, type (n or p), and stability, the latter ideally achieved by covalent bonding of substitutional impurities. Without doubt, large scale application of TMDs in novel devices is to be enabled through dependable and thoroughly controlled manufacturing of synthetic 2D materials. Currently, though, the highest mobility devices incorporating TMDs are realized by making use of micromechanically exfoliated high-quality pristine 2D MoS₂ flakes.^{3,9,10} However, the experimentally established knowledge on reliable chemical doping is still inadequate, specifically regarding the unambiguous dopant identification, quantification, and energy level positioning within the MoS₂ bandgap.

While not left indifferent in the past, the research interest—both theoretically and experimentally—in the understanding and realization of appropriate, well steered doping of MoS₂, in 2D as well as in 3D form, has geared up steadily over the recent years, the effort being accelerated by the strive for 2D applications. First principle calculations using density functional theory have been carried out for various impurities in monolayer 1H MoS₂ (Refs. 11–19) and bulk MoS₂,^{13,19–22} and in various works the nature of chemical dopants has been investigated experimentally,^{21,23–33} with several studies focusing on the realization of a 2D diluted magnetic semiconductor through doping by transition metals.^{29,30} In general, the experimental studies concur that

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adequate n-type doping of MoS₂ can be achieved by incorporation of Re impurities substituting for Mo,²⁷ well corroborated by theoretical insight.^{11,13} In a separate work on effectuating low-resistivity metal-semiconductor contacts, high n-type doping of few-layer exfoliated MoS₂ flakes has been obtained by means of a molecular doping technique (soaking in 1,2-dichloroethane), the doping mechanism being tentatively ascribed to Cl atoms occupying preexisting S vacancies.³³

On the other hand, chemical p-type doping has already been demonstrated back in the 1970s, based on electron spin resonance (ESR) studies, establishing substitutional Zr, Nb, As, and V in 3R MoS₂ grown by chemical vapor transport^{23,24} and As in natural 2H-MoS₂ (Ref. 24) to behave as acceptors. Regarding Nb, the p-type behavior has recently been confirmed experimentally^{25,26} and corroborated theoretically.¹¹ A recent low-temperature (*T*) ESR study has demonstrated As to behave as a very shallow acceptor with activation energy $E_a = 0.7 \pm 0.2$ meV in natural 2H-MoS₂,³¹ and in related ESR work on the same material, it has been concluded that Pb impurities operate as acceptors,²⁸ with Pb likely substituting for Mo.

Additionally, p-type doping by P ion implantation was demonstrated for field effect transistors with ~20 nm thick channels of exfoliated MoS₂,²¹ and a remote N₂ plasma surface treatment has also been put forward by a recent study as an efficient strategy for p-type nitrogen doping of exfoliated MoS₂ flakes.³² Remarkably, other work from the same group concluded that geological MoS₂ may even incorporate both n- and p-type regions within a single sample.³⁴ Finally, very recent work³⁵ has reported on p-type doping resulting from MoS_xO_{3-x} inclusions introduced in MoS₂ films (1.5 nm thick) grown by physical vapor deposition after exposure to oxygen.

In recent ESR work,^{36,37} we reported on the observation and identification of the N acceptor in 2H-MoS₂, the N substituting for an S site. In extending on these results and with the aim to further fundamental insight, we here present the results of an extensive multifrequency ESR study carried out over three observational frequencies and a wide *T* range, in combination with thermal treatment in H₂ and vacuum. Besides basic ESR spectral characterization, attention is focused on the dopant's thermal stability and consolidation of the thermal activation energy. The nitrogen dopant, substituting for S, is reliably established as an adept shallow and stable substitutional acceptor.

II. ESR ON N ACCEPTOR IN MoS₂: SYNOPSIS

In overview, two ESR signals have been related with N impurities in synthetic 2H-MoS₂,³⁶ both exhibiting distinct anisotropy with respect to the angle φ_B that the applied magnetic field, **B**, makes with the *c*-axis (sample main face normal **n**). The most prominent one is illustrated in Fig. 1, showing an X-band observation made at 77 K for **B** along the “high-symmetry” crystal direction **n** (*c*-axis); clearly, the signal emerges as an apparent “three-peak” structure, which, upon deeper examination, unfolds as a symmetric triplet of overlapping lines of total width ~42 G. As illustrated in

FIG. 1. X-band ESR spectrum of N acceptor impurities in synthetic MoS₂, observed for **B**//*c*-axis. The dashed curve superposed on the spectrum represents an optimized computer simulation obtained as the sum of a 1:1:1 hf triplet of isoshaped equally intense lines ($\Delta B_{pp} = 13.6 \pm 0.5$ G; Gaussian shape) superimposed on a central line ($\Delta B_{pp} = 15.3 \pm 0.5$ G; intensity ~26% of the total spectrum; Gaussian shape) centered at (close to) the same $g = 2.032 \pm 0.002$. The small signals emerging at $g = 2.00229$ and $g = 1.99896$ originate from co-mounted marker samples LiF:Li and Si:P, respectively.

Fig. 2(b), a virtually identical spectrum, regarding both shape and width, is recorded at K-band frequency, which has led to the conclusion of the triplet structure to originate from hyperfine (hf) interaction of the unpaired electron spin with a single nucleus of spin $I = 1$; the alternative possibility for the overall signal structure to be of more powder pattern nature is ruled out.

Computer-assisted analysis indicates that the **B**//**n** spectrum may be appropriately fitted [dashed curves in Figs. 1 and 2(b)] as a weighed sum of an isoshaped (Gaussian; $\Delta B_{pp} = 13.6 \pm 0.5$ G) 1:1:1 triplet of hf splitting constant $A_{||} = 14.7 \pm 0.2$ G superimposed on a single central line (CL) of $\Delta B_{pp} = 15.3 \pm 0.5$ G (Gaussian), both centered at (close to) the same g value ($g_{||} = 2.032$). The triplet and CL shift in tandem as φ_B is varied, indicating a common defect origin. The totality of the spectrum corresponds to an impurity density of $(2.3 \pm 0.2) \times 10^{17} \text{ cm}^{-3}$, of which the CL accounts for ~26%. The latter density appears uniform over the mm-size scale (2–7 mm main sample size).

Guided by further analysis, the main triplet has been assigned as a single ¹⁴N hf splitting originating from isolated N impurities in MoS₂. Furthermore, the signal is found to exhibit axial symmetry characterized by $g_{||} = 2.032 \pm 0.002$ and $g_{\perp} = 2.270 \pm 0.002$ —a kind of anisotropy, i.e., magnitude of g ($>g_e = 2.00232$, the free electron value) and $|g_{\perp} - g_{||}|$, and symmetry about the *c*-axis, typical for covalently bonded substitutional impurities in MoS₂ behaving as acceptors, as previously established for As (substituting for S),^{24,31} Nb, Zr, and V.²³ This has led to the assignment of the observed ESR signal to N acceptors substituting for S vacancies, in line with previous theoretical insight.^{11,12}

For illustrative reasons, a more in-depth spectroscopic exposure of the explicit anisotropy of the main N impurity signal,

FIG. 2. (a) K-band ESR spectra of the N impurity observed at 77 K at various values of φ_B for $\mathbf{B}$ rotating over an angle of 90° with respect to the c -axis. The signals for $\varphi_B = 0^\circ$ and 90° are characterized by $g_\perp = 2.270 \pm 0.002$ [spectrum (1)] and $g_\parallel = 2.032 \pm 0.002$ [spectrum (2)], respectively. The hf triplet and CL appear to shift in tandem, indicating a common defect origin and, notably, the hf triplet, of total width ~ 42 G as indicated by the dotted lines, observed for $\mathbf{B} \parallel \mathbf{n}$ is narrowed down to become enclosed in a single, seemingly structureless, intense signal of peak-to-peak width $\Delta B_{pp} = 4.8 \pm 0.2$ G for $\varphi_B \rightarrow 90^\circ$ ($\mathbf{B} \perp \mathbf{n}$), suggesting significant anisotropy of the hf matrix. (b) A zoomed-in comparison of the $\varphi_B = 0^\circ$ and $\varphi_B = 90^\circ$ responses observed over narrow field scans. The dashed curve superposed on spectrum (2) represents an optimized computer simulation obtained as the sum of a 1:1:1 hf triplet of isoshaped equally intense lines superimposed on a central line centered at (close to) the same $g = 2.032 \pm 0.002$.

regarding both shape and g value, is provided in Fig. 2(a) showing the main N signal recorded at 77 K (K-band) for six different angles φ_B ranging from 0° to 90° (corresponding to $\mathbf{B} \parallel \mathbf{n}$ and $\mathbf{B} \perp \mathbf{n}$, respectively). Clearly, as mentioned before, the hf triplet and the central line tightly shift in tandem, indicating a common defect origin. Also, it appears that the hf splitting matrix possesses a relatively high level of anisotropy as the hf triplet strongly narrows down to become comprised within a single, seemingly structureless, intense peak of peak-to-peak width $\Delta B_{pp} = 4.8 \pm 0.2$ G for $\varphi_B \rightarrow 90^\circ$ ($\mathbf{B} \perp \mathbf{n}$). The strikingly strong anisotropy of the overall signal shape is fully exposed in “enlarged view” in Fig. 2(b), showing a comparison of narrow field sweep K-band spectra observed at 77 K for the “extreme” field orientations, i.e., $\mathbf{B} \perp \mathbf{n}$ and $\mathbf{B} \parallel \mathbf{n}$ [signal (1) and (2), respectively].

In analogy with previous work,^{38,39} the CL part of the total spectrum suggests some nonuniform doping with $\sim 26\%$ of the N dopants not residing in the preferred “isolated” doping state. Indeed, similar to the case of n-type P doping in Si, the appearance of the central line would correspond to exchange coupled electrons at clustered dopant impurities (mostly pairs) resulting in averaging out of the ^{14}N hf splitting with the electrons now acting as one unit.^{38,39} This interpretation is further corroborated by the observed second ESR signal, i.e., a correlated (i.e., regarding anisotropy and signal shape) single half field line (characterized by $g_\perp = 3.92 \pm 0.01$, $\Delta B_{pp} = 9 \pm 1$ G at 4.2 K for $\mathbf{B} \perp \mathbf{n}$, and an intensity of $\sim 0.6\%$ of the main signal) indicative of the presence of $S \geq 1$ centers (N dopant clusters).

Finally, it should be noticed that, since no particular doping process has been applied, the incorporation of N impurities must be sample growth related.

III. EXPERIMENTAL DETAILS

A. Samples

The examined specimen is a commercial bulk synthetic 2H-polytype MoS₂ crystal of, as specified by the supplier,⁴⁰ 99.995% purity, grown by chemical vapor deposition (CVD) using high-purity Mo and sulfide sources. A thermoelectric test demonstrated the sample to be manifest p-type. From the mother crystal, thin (~ 0.2 – 0.4 mm) ESR-appropriate slices of $\sim 2 \times 7$ mm² main area were cut, with the c -axis along $\mathbf{n}$.

Measurements were carried out on samples in the as-received state and after thermal treatment in H₂ (~ 1.1 atm) and vacuum ($< 7 \times 10^{-6}$ mbar) for ~ 45 min at selected temperatures in the range 22–500 °C and 500–740 °C, respectively, in order to assess the reactivity and thermal stability of observed ESR-active centers. More specifically, as alluded to in the previous section, the focus is on the N impurities, operating as acceptors. Thermal treatments were performed using a conventional resistively heated furnace system foreseen with a double-walled high-purity quartz insert, as described elsewhere.⁴¹

With applying thermal treatments in H₂, the main goal is the investigation of the potential inactivation (passivation) of the acceptors through binding to H [an effect well known for some dopants in other semiconductors (see, e.g., Ref. 42)]. In a next sequence, this is followed by the analysis of their potential reactivation (acceptor-hydrogen dissociation) under annealing in vacuum, herewith, at the same time, intending to provide useful information on the overall thermal stability—as functional dopants—of the substitutional covalently bonded acceptors. The thermal treatment analysis was carried out by applying a series of thermal steps sequentially on one sample, at incremental T , in order to expose the evolution of the thermal impact, and potentially, reveal any abrupt transitions.

Additionally, it may be useful to add that over all the thermal treatments applied, no creation or activation of additional “new” ESR signals was noticed.

B. ESR spectroscopy

Conventional continuous-wave absorption first derivative X- (~ 8.9 GHz), K- (~ 20.4 GHz), and Q-band (~ 34.3 GHz) ESR

measurements were carried out at temperatures ranging from 4.2 to 298 K using periodic modulation, $B_m \cos(\omega_m t)$, at $\omega_m/2\pi \approx 100$ kHz of **B**. The accurate determination of defect densities and g values of the observed signals was aided by employing two co-mounted calibrated marker samples, i.e., LiF:Li ($g = 2.002293 \pm 0.000002$; spin $S = 1/2$)⁴³ and Si:P [$g(4.3 \text{ K}) = 1.99869 \pm 0.00002$; $S = 1/2$].⁴⁴ Defect densities were reliably obtained by double numerical integration of the observed dP_{μ}/dB signals (P_{μ} the reflected microwave power) where care was taken to record spectra under distortion-avoiding spectrometer settings, i.e., appropriately restricted B_m and incident microwave power P_{μ} (see, e.g., Ref. 45 for spectroscopic details). The signal anisotropy was monitored by varying the angle φ_B over a range of $\sim 180^\circ$.

IV. RESULTS AND DISCUSSION

A. ESR spectrum

1. Temperature dependence

Aside from the highly anisotropic overall signal shape, as aforementioned, the observational temperature also strongly

affects the appearance of the N acceptor signal, as illustrated in Fig. 3, showing K- [panel (c)] and Q-band [panel (d)] spectra recorded for **B** $\perp$ **n** and **B**//**n**, respectively, over a broad T range (4.2–298 K). A similar trend of signal broadening with increasing T , which can be primarily ascribed to a raising spin–lattice interaction (T_1 relaxation), is observed for both orientations, reaching strong line broadening at high temperatures ($T \gtrsim 200$ K). As a result, with increasing temperature in this T range, the observability (signal-to-noise ratio) of the ESR signal is gradually reduced, which is further lowered due to the expected Curie-type susceptibility behavior, $\chi \propto 1/T$, and the decreasing amount of neutral, ESR-active, acceptors due to dopant activation. With raising T , these mechanisms make it thus gradually more troublesome to reliably distinguish the targeted signal from relatively “growing” omnipresent (cavity) background responses as illustrated in Fig. 3(d) (Q-band observations): Here, for one, the hf pattern (first, second, and third lines) of ⁵⁵Mn isotope ($I = 5/2$) impurities is seen to come out relatively more prominent with increasing T . As a result, when ESR monitoring the density of activated dopants (see below), this obfuscating trend will require an especially cautious double

FIG. 3. Temperature dependence of the global linewidth of the first derivative K-band (a) and Q-band (b) N acceptor signal observed in as-received synthetic 2H MoS₂ for **B** $\perp$ **n** and **B**//**n**, respectively, over the T range 4.2–298 K. Starting from a plateau value and remaining constant for $T \lesssim 75$ K, the linewidth reaches a minimum value of $\Delta B_{pp} = 3.2 \pm 0.2$ G at an intermediate temperature of ~ 105 K for **B** $\perp$ **n** (a), while for **B**//**n** (b) a minimum total linewidth of $\Delta B_{pp} = 17 \pm 2$ G is achieved at a similar ~ 125 K. For higher temperatures, the signal width is seen to grow rapidly. The evolution of the signal shape of the K-band (**B** $\perp$ **n**) and Q-band (**B**//**n**) N acceptor ESR spectra is shown in (c) and (d), respectively. The seemingly structureless single signal for **B** $\perp$ **n** at low T undergoes distinct broadening with increasing T , ascribed to the raising spin–lattice interaction (T_1 relaxation). A similar signal broadening is observed for both orientations, as expected. Additional background signals, such as the hf pattern (first, second, and third lines) of ⁵⁵Mn ($I = 5/2$) cavity background impurities gradually arise more prominently in the Q-band spectra (d) due to the severe broadening and, accordingly, apparent fading of the N signal at high T .

numerical integration routine to obtain trustworthy data at temperatures approaching room temperature.

The detailed T dependence of the linewidth at K-band for $\mathbf{B} \perp \mathbf{n}$, shown in Fig. 3[panel (a)], exposes a minimum peak-to-peak linewidth of $\Delta B_{pp} = 3.2 \pm 0.2$ G reached at ~ 105 K. Similarly, the T dependence of the global (total) linewidth at Q-band for $\mathbf{B} // \mathbf{n}$ is shown in Fig. 3(b), revealing a minimum total linewidth of $\Delta B_{pp} = 17 \pm 2$ G at ~ 125 K. As exposed, the trend is similar for both cases: Starting from the low- T end, the width remains constant (plateau value) up to ~ 75 K, to narrow down and reach a minimum at ~ 105 – 125 K from whereon the signal steadily broadens fastly with raising T . The temperature at which the minimum linewidth is reached seems similar for both orientations, despite the linewidth being slightly more precarious to determine at Q-band for $\mathbf{B} // \mathbf{n}$ due to an, albeit modestly, changing overall signal shape. The observation of a minimum linewidth at an intermediate temperature is indicative of the presence of one (or more) broadening mechanisms in addition to the common T_1 relaxation. Further investigation on the appropriate relaxation mechanisms is set aside for future work.

2. Saturation

Another useful spectral characteristic that may assist in defect identification is the ESR saturability. In the search for similarities, the saturability of the current N main signal has been compared to that of the previously studied As signal in geological MoS₂.³¹ Continuous-wave saturation curves of both signals were recorded by inserting two MoS₂ samples, i.e., the geological (As containing) and synthetic (N dopant) one, in the spectrometer cavity together with some crushed HSQ200-type fused quartz⁴⁶ [[OH] <30 ppm (other impurities) <20 ppm] and, for reference, a Si:P marker.⁴⁴

Figure 4 shows the derivative amplitude A_{pp} , normalized in the nonsaturation regime, i.e., $B_1 < 10^{-4}$ G, for each ESR signal as a function of B_1 , the amplitude of the magnetic microwave field at the sample position in the cavity, derived from the incident microwave power P_μ and quality factor Q . The data are mutually normalized in the nonsaturation regime, i.e., $B_1 < 10^{-4}$ G. All measurements were performed at 4.2 K with $\mathbf{B} \perp \mathbf{c}$ -axis for both MoS₂ samples. Figure 4 convincingly demonstrates the distinctly different relaxation behavior of the four ESR signals with the Si:P and E' defect (generic entity $\text{O}_3 \equiv \text{Si} \cdot$) signal, the latter stemming from the crushed fused quartz sample, exhibiting the expected previously reported behavior.⁴⁷ The Si:P signal is nonsaturating over the whole B_1 range covered, while the E' response shows high saturability. Pertinently, the saturation curves of the N and As acceptor signals are manifestly different despite their respective densities and substitutional position in the crystal lattice being similar. But this may be according to expectations. Indeed, as the saturation behavior is governed by the product $T_1 T_2$,⁴⁸ with T_1 being the spin–lattice relaxation time and T_2 the spin–spin relaxation time, the stronger spin–orbit coupling of As as compared to that of N results in a better coupling to the lattice and, consequently, saturation sets in at a higher incident microwave power level

Fig. 4. Comparison of continuous-wave saturation data measured at 4.2 K for four ESR signals. This includes the main N signal measured on the current synthetic MoS₂ specimen in the as-received state, the As acceptor signal from a geological MoS₂ sample, the E' signal in crushed fused SiO₂, and, for reference, the Si:P marker signal, represented by filled circles, unfilled squares, diamonds, and circles, respectively. Both the E' and Si:P marker signal (the latter not saturating) exhibit the expected saturation behavior. While the N acceptor's saturation curve appears to reach a maximum value at ~ 0.02 G corresponding to T_1 (4.2 K) $\approx 3 \times 10^{-4}$ s, the As acceptor's signal does not saturate over the B_1 range covered, indicating, for comparable signal widths, a distinctly smaller T_1 value compared to N.

for the As acceptor signal. Therefore, the As signal data in Fig. 4 display only marginal saturation over the B_1 range covered. The exhibited resonant microwave saturation behavior is thus found in line with the assigned N and As acceptor signal nature.

In contrast with the As signal, the E' signal shows a maximum signal height at $\sim 10^{-3}$ G, as expected,⁴⁷ while the N signal tends to reach a maximum value of the saturation curve outside of the B_1 range covered. Yet, from the trend of the N saturation curve, the maximum value can be estimated as $B_1 \approx 0.02$ G. According to theory,⁴⁹ the maximum of the saturation curve corresponds to

$$B_1^2 \gamma^2 T_1 T_2 \approx \frac{1}{2}, \quad (1)$$

where $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio, with μ_B being the Bohr magneton and $2\pi\hbar$ Planck's constant, and

$$T_2 = \frac{2}{\sqrt{3}\gamma\Delta B_{pp}}, \quad (2)$$

resulting in T_1 (4.2 K) $\approx 3 \times 10^{-4}$ s for the N center.

B. Thermal treatment: Dopant stability

Aiming at a better understanding of dopant stability, the N acceptor was subjected to two series of thermal treatments, one first performed in H₂ (1.1 atm), and the other in high vacuum. Thermal steps were performed sequentially on the same sample physically, priorly subjected to a “reference”

FIG. 5. Effect of applied thermal treatments in H₂ (1.1 atm; ~45 min) and vacuum ($<7 \times 10^{-6}$ mbar; ~45 min) on the N acceptor signal observed in synthetic MoS₂ for $\mathbf{B} \perp \mathbf{c}$ -axis. The spectrum in the center of the figure represents the N impurity signal of the initial sample (as-received sample subjected to vacuum anneal at ~360 °C). The upper spectra (upper blue rectangle) show the passivation effect in H₂ ambient with increasing T_{an} while the bottom spectra (lower red rectangle) display the evolution of the signal in vacuum with increasing T_{an} .

setting treatment in vacuum (~360 °C; ~2 h)—referred to as the initial state. Figure 5 shows an overview of observed ESR spectra over the various thermal steps applied, whereas, in quantitative terms, Fig. 6 presents the evolution of the ESR signal intensity (non-activated N acceptor density). Various trends are revealed: As to thermal treatment in H₂, the N signal is seen to remain unaffected, within experimental accuracy, for heating temperatures (T_{an} s) up to ~370 °C, to then drop drastically by 1 order of magnitude for T_{an}

FIG. 6. Evolution of the N impurity signal intensity, normalized to the initial intensity value (black circle), after subsequent thermal treatments in H₂ (blue squares) and vacuum (red diamonds). While the signal appears not affected (within experimental accuracy) by treatment in H₂ up to ~370 °C, a drastic drop in signal intensity (~1 order of magnitude) occurs at ~500 °C, tentatively ascribed to passivation of N acceptors by bonding to H. As the signal intensity after thermal treatments in vacuum does not increase significantly, the depassivation procedure proves to be unsuccessful. The dashed curves guide the eye.

reaching 500 °C. Building on previous experience with inactivation of point defects in semiconductors, such as B acceptors in Si,⁴² this might be ascribed to direct passivation (inactivation) of N acceptors through defect-H bond formation.

Also guided by previous knowledge, one may then quest for possible reactivation of N dopants, i.e., defect-H bond breaking, under thermal treatment in vacuum—the intent of the second series of thermal steps applied. The data, also compiled in Fig. 6, show that, perhaps apart from a small initial increase, the vacuum treatments have little effect on the passivated N signal: no signal reactivation occurs up to $T_{an} = 645$ °C. Along conventional interpretation [see, e.g., Ref. 50 and references therein], this failing impact of vacuum treatment may be seen as a result of strong defect-H bonding, resulting in an activation energy ($E_{act} \gtrsim 3.3$ eV) too high to enable any significant dopant reactivation up to ~645 °C. Here, theoretical analysis and computational modeling may provide further insight.

However, further increasing T_{an} to 740 °C results in one more order of magnitude decrease in signal intensity. This “opposite,” quite counterintuitive effect from vacuum treatment likely refers to fatal disruption of the substitutional N acceptor configuration through atomic displacement(s) and/or complex formation with other embedded impurities or intrinsic defects, resulting in a distorted point defect of distinctly different electrical behavior.

The latter observations may expose major implications for the application of N-doped MoS₂ in novel nanoelectronic devices as once the N acceptor is passivated by hydrogen, it cannot be depassivated through a thermal treatment in vacuum at temperatures up to ~740 °C.

C. Activation energy

Besides serving as an exclusive technique to atomically identify and quantify a dopant impurity from its unique ESR spectrum, ESR also acts as a most useful technique to determine the dopant-type specific activation energy. An important factor determining the suitability of a dopant to be incorporated in a semiconductor material intended for novel nanoelectronic devices is its activation energy which, for an acceptor, can be written as $E_a = E_A - E_v$ with E_A being the acceptor energy level and E_v the valence band (VB) maximum. The activation energy can be reliably determined by monitoring the signal intensity, which is proportional to the ESR-active dopant density, versus T together with, for analysis, the proper mathematical expression for the dopant occupation versus T , derived within the standard semiclassical solid state theory of band structure, as discussed before^{31,51} for well-defined conditions. Additionally, it is of utmost importance in this process to take into account the intrinsic T dependence of the signal intensity due to the specific magnetic behavior (susceptibility χ) of the acceptor spin system.³¹

As elaborated in previous work,³¹ one would preferably aim to monitor the intensity of, if emerging, the (primary) hf structure originating from and known to be distinctive for sparsely distributed decoupled dopants, the latter standing

for the desired doping configuration, of which the corresponding spin system exhibits Curie-type susceptibility $\chi \propto 1/T$. In this way, the impeding influence of other spectral components with a potentially unclear T -dependent χ is prevented. Currently, we would therefore preferably direct our attention to the intensity monitoring of only the ^{14}N hf triplet. Unfortunately, this strategy turns out to be unreliable due to considerable spectral overlap, especially for the range $T \gtrsim 100$ K. Therefore, the intensity of the entire spectrum has been monitored instead, resulting in a procedure that is nonetheless considered reasonable and acceptable as the additional CL not only makes up a rather small fraction ($\sim 26\%$) of the entire N ESR signal but most likely also exhibits a (close to) $\chi \propto 1/T$ behavior, as previously demonstrated for P donors in Si at high doping levels.^{38,44}

Directed by the approaches at hand for solid state theory based computational modeling of dopant occupation statistics, in analyzing and interpreting data, three T ranges are discussed separately: First the entire T range covered (4.3–298 K), second the low- T regime ($T \lesssim 150$ K), and finally, the high- T data ($T \gtrsim 130$ K). All data, taken on as-received samples, have been corrected for the admitted $\chi \propto 1/T$ dependence in the subsequent analyses.

1. Entire T range

The obtained intensity versus T plot is shown in Fig. 7 for K- [panel (a)] and Q-band [panel (b)] data. For analysis, one can derive an expression from dopant occupation statistics for the ratio of the neutral, ESR-active, acceptor density N_A^* to the total acceptor density N_A ^{31,51}

$$\frac{N_A^*}{N_A} = 1 - \frac{2}{1 + \sqrt{1 + K e^{E_a/kT}}}, \quad (3)$$

where $K = 4g_d N_A / N_v = (4g_d N_A / N_{v0}) T^{-3/2} \equiv K_0 T^{-3/2}$, and $N_v = 2(2\pi m_v kT/h^2)^{3/2} \equiv N_{v0} T^{3/2}$ is the VB effective density of states, g_d represents the impurity level spin degeneracy factor inserted for bulk MoS₂ as $g_d = 2$ since there appears to be no band degeneracy at the top of the VB,^{51,52} m_v is the hole effective mass, tabulated for MoS₂ as $m_v = 0.56m_0$,^{52,53} with m_0 being the electron rest mass, k is Boltzmann's constant, and h is Planck's constant. The VB effective density of states is obtained as $N_{v0} \approx 2.02 \times 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2}$. Equation (3) is valid for the conditions of doping absolutely governed by one kind of dopant with negligible compensation or intrinsic excitation, and a semiconductor nondegenerate throughout the whole T range covered. It seems reasonable to assume that for the current p-type MoS₂ material, the N acceptor is the far dominant type of dopant, appearing in a density that would dependably meet the condition of nondegeneracy,²⁶ and supposedly also that of negligible compensation.

From optimized fitting of Eq. (3) to the K-band data in Fig. 7(a) (cf. dashed curve), we obtain $E_a(K) = 45 \pm 7$ meV, unveiling the N acceptor as a shallow dopant. Applying Eq. (3) to the Q-band data in Fig. 7(b) reveals an activation energy $E_a(Q) = 50 \pm 10$ meV, firmly consolidating the value obtained for K-band. Noteworthy is the comforting

Fig. 7. Temperature dependence of the K- (a) and Q-band (b) intensity (double integral of dP_{μ}/dB spectra; $B \perp c$ -axis) of the ESR signal ascribed to N acceptor atoms substituting for S in synthetic MoS₂. The data, recorded over the T range 4.2–298 K, are normalized to the low- T plateau value ($T \lesssim 50$ K) after correction for the admitted $\chi \propto 1/T$ dependence. Error bars denote the spread in the data of multiple observations. The dashed curves represent an optimized fitting of Eq. (3), resulting in much similar activation energies $E_a = 45 \pm 7$ meV and 50 ± 10 meV for K- and Q-band, respectively.

agreement of the emerging fitting values for the prefactors $K_0(K) = (7 \pm 4) \times 10^2 \text{ K}^{-3/2}$ and $K_0(Q) = (2 \pm 1) \times 10^3 \text{ K}^{-3/2}$, for the K- and Q-band analysis, respectively, with the “expected” value, $\sim 9 \times 10^2 \text{ K}^{-3/2}$, calculated from the values specified for N_{v0} , g_d , and, notably, the ESR-inferred N_A value. The $K_0(Q)$ value is somewhat less close. Accordingly, and within the conviction that, on spectroscopic grounds, the attained overall K-band data set on the monitoring of the N signal intensity versus T is more accurate than the Q-band one, the inferred $E_a(K) = 45 \pm 7$ meV is advanced as most reliable and will be quoted that way.

The self-consistency of the prefactors, together with the overall excellent fitting of the data and reassuring agreement of the K-band and Q-band results, provides confidence in the appropriateness of the applied interpretation approach [i.e., Eq. (3)]. Moreover, in combination with the value previously measured³¹ for As, i.e., $E_a(\text{As}) = 0.7 \pm 0.2$ meV, the results obtained for $E_a(\text{N})$ are consistent with the theoretical prognosis for group V p-type dopants in MoS₂ (Ref. 11)—albeit

calculated for the monolayer form—in that $E_a(N)$ is projected to be substantially larger (>1 order of magnitude) than $E_a(As)$.

A final remark to be added regarding the inferred N acceptor activation energy is that E_a has been obtained through monitoring the intensity of the entire N acceptor spectrum, i.e., the added signals of both the isolated N acceptors and the one, as outlined before, ascribed to clustered N dopants. If both species, as likely, would be characterized by somewhat dissimilar E_a values, the inferred activation energy, advanced as pertaining to the isolated acceptors, may be affected by some averaging over both species. Yet, as the clustered part constitutes only a fraction of $\sim 26\%$ of the total N signal, the influence might turn out to be rather limited.

2. Low- T range

Next, inspired by a conventional custom, we focused on the separate fitting of only the low- T range data of the N signal

FIG. 8. Low- T ($T \lesssim 150$ K) temperature dependence of the K- (a) and Q-band (b) intensity of the N impurity signal observed in synthetic MoS₂ for B_{LC} -axis. The signal intensity is normalized to the low- T plateau value ($T \lesssim 50$ K) after proper correction for the admitted $\chi \propto 1/T$ dependence. The dashed curves represent an optimized fitting of Eq. (5), resulting in an activation energy $E_a = 33 \pm 11$ meV and 57 ± 18 meV for K- and Q-band, respectively. Error bars denote the spread in the data of multiple observations.

intensity versus T monitoring, presented in Fig. 8 for K- [panel (a)] and Q-band [panel (b)] measurements. For the low- T condition, when relatively few holes are excited, $K_{\text{exp}}(E_a/kT) \gg 1$ (say >10), translating in the current case to $T \lesssim 150$ K, Eq. (3) approximates to

$$\frac{N_A^*}{N_A} = 1 - \sqrt{N_v/g_d N_A} e^{-E_a/2kT} \equiv 1 - K'_0 e^{-E_a/2kT}, \quad (4)$$

which can be rewritten as

$$(1 - N_A^*/N_A)T^{-3/4} \equiv K'_0 e^{-E_a/2kT}, \quad (5)$$

with $K'_0 \equiv \sqrt{N_v/g_d N_A}$.^{31,51} A convenient feature of Eq. (5) is that E_a would be directly provided by the slope of the straight line fitted to the plot $\ln[(1 - N_A^*/N_A)T^{-3/4}]$ versus $1/T$.⁵¹ Fitting the K- and Q-band low- T data, shown in Figs. 8(a) and 8(b), respectively, with Eq. (5) an activation energy $E_a(K) = 33 \pm 11$ meV is obtained for the K-band

FIG. 9. High- T ($T \gtrsim 130$ K) temperature dependence of the K- (a) and Q-band (b) intensity of the N acceptor signal for B_{LC} -axis. The data have been normalized to the low- T plateau value ($T \lesssim 50$ K) after appropriate $\chi \propto 1/T$ dependence correction. Error bars denote the spread on the data of multiple observations. The dashed curves show an optimized fitting of Eq. (6) to the intensity data, resulting in an activation energy $E_a = 29 \pm 12$ meV and $E_a = 20 \pm 12$ meV for K- and Q-band, respectively.

measurements and, in decent agreement, $E_a(Q) = 57 \pm 18$ meV for the Q-band observations. Furthermore, the obtained prefactor values $K'_0(K) = 0.03 \pm 0.02 \text{ K}^{-3/4}$ and $K'_0(Q) = 0.05 \pm 0.04 \text{ K}^{-3/4}$ for K- and Q-band, respectively, are both remarkably close to the value $\sim 0.07 \text{ K}^{-3/4}$ calculated using the estimated N_{v0} , g_d and measured N_A . To be added here is that the obtained E_a value from the low- T data, though in fair agreement with the “overall” fitting results [cf. Eq. (3)], may be somewhat less reliable as the fitting procedures encompass fewer data points.

3. High- T range

Finally, in seeking further consolidation, we may address fitting of data to a separate mathematical description specifically derived for the high- T part of the occupation of the acceptor dopants.⁵⁴ For the usual conditions of absolute dominant doping by one kind of dopant, negligible compensation and intrinsic excitation, it has been derived that for $E_F - E_A \gg kT$ (say $\gtrsim 3kT$, with E_F the Fermi level)

$$\begin{aligned} \frac{N_A^*}{N_A} &= \left(1 + \frac{N_v}{g_d N_A} e^{-E_a/kT} \right)^{-1} \\ &\equiv (1 + K''_0 T^{3/2} e^{-E_a/kT})^{-1}, \end{aligned} \quad (6)$$

with $K''_0 = (N_{v0}/g_d N_A) = (K'_0)^2$.^{31,51} Optimized fitting of Eq. (6) to the high- T data ($T \gtrsim 130$ K) shown in Fig. 9 results, for the K-band data [panel (a)], in $E_a = 29 \pm 12$ meV, with $K''_0 = (4 \pm 3) \times 10^{-3} \text{ K}^{-3/2}$ and for Q-band [panel (b)] in a similar $E_a = 20 \pm 12$ meV, and $K''_0 = (8 \pm 6) \times 10^{-4} \text{ K}^{-3/2}$. The prefactor K''_0 , especially for K-band, is found to be close to the calculated value $\sim 7 \times 10^{-3} \text{ K}^{-3/2}$, adding to the self-consistency. Once again, the obtained E_a value from the high- T data is, while still in fair agreement with the “overall” fitting result obtained via Eq. (3), deemed somewhat less reliable as the fitting routine encompasses even fewer data points than the low- T analysis.

V. SUMMARY AND CONCLUSION

In summary, a multifrequency ESR study over the T range 4.2–298 K has resulted in the identification of the N acceptor dopant substituting for S sites in 2H-polytype synthetic bulk MoS₂ crystals with a density of $(2.3 \pm 0.2) \times 10^{17} \text{ cm}^{-3}$. Substantial N contamination is thus revealed as an inherent trait of the specific CVD method applied for MoS₂ synthesis.

The N acceptor ESR spectrum is mainly composed of a primary ¹⁴N hf structure making up only $\sim 74\%$ of the total spectrum, superimposed on a central line, revealing some nonuniform doping with $\sim 26\%$ of the N dopants not residing in the preferred “isolated” doping state. The agglomeration of the N dopants is further supported by the observation of a half field line, indicative for the presence of an $S \geq 1$ spin system. A comparison of the saturation behavior of the N acceptor in synthetic MoS₂ with the As acceptor in natural MoS₂ also revealed that the N signal saturates at a much lower incident power level, corresponding to T_1 (4.2 K) $\approx 3 \times 10^{-4}$ s. This different behavior can be attributed to the

stronger spin–orbit coupling, and consequently better coupling to the crystal lattice, of the As center compared to the N center.

Assessing the stability of the N dopant, a variety of thermal treatments revealed drastic inactivation (passivation) of the N acceptor when exposed to an H₂ ambient at ~ 500 °C. Reactivation in vacuum of the N acceptor at temperatures up to ~ 740 °C appeared unsuccessful, urging great caution with respect to doping efficiency when exposing N-doped MoS₂ to H₂ at relatively high temperatures of $\gtrsim 500$ °C.

Finally, device-electronically most relevant, extensive monitoring of the T-dependent ESR intensity at K- and Q-band revealed the N dopant as a shallow acceptor with an activation energy of $E_a = 45 \pm 7$ meV, uncovering N as an adequate candidate for stable covalently bonded p-type doping of bulk MoS₂.

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- ¹Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* **7**, 699 (2012).
- ²D. Voiry, A. Mohite, and M. Chhowalla, *Chem. Soc. Rev.* **44**, 2702 (2015).
- ³B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, *Nat. Nanotechnol.* **6**, 147 (2011).
- ⁴I. Song, C. Parkab, and H. C. Choi, *RSC Adv.* **5**, 7495 (2015).
- ⁵S. McDonnell, R. Addou, C. L. Hinkle, and R. M. Wallace, in *2D Materials for Nanoelectronics*, edited by M. Houssa, A. Dimoulas, and A. Molle (Taylor & Francis, Boca Raton, FL, 2016), p. 163.
- ⁶A. H. Castro Neto and K. Novoselov, *Mater. Express* **1**, 10 (2011).
- ⁷J.-G. Song *et al.*, *Nat. Commun.* **6**, 7817 (2015).
- ⁸A. K. Geim and I. V. Grigorieva, *Nature* **499**, 419 (2013).
- ⁹R. Ganatra and Q. Zhang, *ACS Nano* **8**, 4074 (2014).
- ¹⁰X. Cui *et al.*, *Nat. Nano* **10**, 534 (2015).
- ¹¹K. Dolui, I. Rungger, C. Das Pemmaraju, and S. Sanvito, *Phys. Rev. B* **88**, 075420 (2013).
- ¹²Q. Yue, S. Chang, S. Qin, J. Li, *Phys. Lett. A* **377**, 1362 (2013).
- ¹³H.-P. Komsa and A. V. Krashenninnikov, *Phys. Rev. B* **91**, 125304 (2015).
- ¹⁴M. S. Wu, B. Xu, G. Liu, and C.-Y. Ouyang, *Acta Phys. Sin.* **62**, 037103 (2013).
- ¹⁵H. Shu, P. Luo, P. Lang, D. Cao, and X. Chen, *ACS Appl. Mater. Interfaces* **7**, 7534 (2015).
- ¹⁶D. Ma, W. Ju, T. Li, X. Zhang, C. He, B. Ma, Y. Tang, Z. Lu, and Z. Yang, *Appl. Surf. Sci.* **364**, 181 (2016).
- ¹⁷Y. C. Cheng, Z. Y. Zhu, W. B. Mi, Z. B. Guo, and U. Schwingenschloegl, *Phys. Rev. B* **87**, 100401R (2013).
- ¹⁸A. Ramasubramaniam and D. Naveh, *Phys. Rev. B* **87**, 195201 (2013).
- ¹⁹A. W. Robertson *et al.*, *ACS Nano* **10**, 10227 (2016).
- ²⁰A. Molle *et al.*, *Adv. Electron. Mater.* **2**, 1600091 (2016).
- ²¹A. Nipane, D. Karmakar, N. Kaushik, S. Karande, and S. Lodha, *ACS Nano* **10**, 2128 (2016).
- ²²O. Brontvein, R. Tenne, and A. Enyashin, *Inorganics* **2**, 363 (2014).
- ²³R. S. Title and M. W. Shafer, *Phys. Rev. Lett.* **28**, 808 (1972).
- ²⁴R. S. Title and M. W. Shafer, *Phys. Rev. B* **8**, 615 (1973).
- ²⁵M. R. Laskar *et al.*, *Appl. Phys. Lett.* **104**, 092104 (2014).
- ²⁶J. Suh *et al.*, *Nano Lett.* **14**, 6976 (2014).
- ²⁷E. D. Brandao, G. M. Ribeiro, P. H. Vaz, J. C. González, and K. Krambrock, *J. Appl. Phys.* **119**, 235701 (2016).
- ²⁸S. Iacovo, A. Stesmans, M. Houssa and V. V. Afanas'ev, *J. Phys. Condens. Matter* **29**, 08LT01 (2017).
- ²⁹C. Huang, Y. Jin, W. Wang, L. Tang, C. Song, and F. Xiu, *J. Semiconductors* **38**, 033004 (2017).
- ³⁰K. Zhang *et al.*, *Nano Lett.* **15**, 6586 (2015).

- ³¹A. Stesmans, S. Iacovo, and V. V. Afanas'ev, *Appl. Phys. Lett.* **109**, 172104 (2016).
- ³²A. Azcatl *et al.*, *Nano Lett.* **16**, 5437 (2016).
- ³³L. Yang *et al.*, *Nano Lett.* **14**, 6275 (2014).
- ³⁴S. McDonnell, R. Addou, C. Buie, R. M. Wallace, and C. L. Hinkle, *ACS Nano* **8**, 2880 (2014).
- ³⁵A. T. Neal, R. Pachter, and S. Mou, *Appl. Phys. Lett.* **110**, 193103 (2017).
- ³⁶B. Schoenaers, A. Stesmans, and V. V. Afanas'ev, *AIP Adv.* **7**, 105006 (2017).
- ³⁷B. Schoenaers, A. Stesmans, and V. V. Afanas'ev, *Phys. Status Solidi C* **14**, 1700211 (2017).
- ³⁸H. Ue and S. Maekawa, *Phys. Rev.* **B3**, 4232 (1971); J. D. Quirt and J. R. Marko, *Phys. Rev.* **B7**, 3842 (1973).
- ³⁹C. P. Slichter, *Phys. Rev. B* **99**, 479 (1955).
- ⁴⁰HQ Graphene, Groningen, The Netherlands.
- ⁴¹A. Stesmans, *Phys. Rev. B* **48**, 2418 (1993).
- ⁴²J. I. Pankove, D. E. Carlson, J. E. Berkeyheiser, and R. O. Wance, *Phys. Rev. Lett.* **51**, 2224 (1983).
- ⁴³A. Stesmans and Y. Wu, *J. Phys. D Appl. Phys.* **21**, 1205 (1988).
- ⁴⁴A. Stesmans, *J. Magn. Reson.* **76**, 14 (1988).
- ⁴⁵J. A. Weil, J. R. Bolton, and J. E. Wertz, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications* (Wiley, NY, 1994), pp. 504–507.
- ⁴⁶Trade name of Heraeus, Inc.
- ⁴⁷A. Stesmans and F. Scheerlinck, *Phys. Rev. B* **51**, 4987 (1994).
- ⁴⁸T. G. Castner, Jr., *Phys. Rev.* **115**, 1506 (1959).
- ⁴⁹C. P. Poole, Jr., *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques* (Dover, NY, 1983), pp. 589–600.
- ⁵⁰A. Stesmans, *Phys. Rev. B* **61**, 8393 (2000).
- ⁵¹J. S. Blakemore, *Semiconductor Statistics* (Pergamon, Oxford, 1962).
- ⁵²E. Scalise, M. Houssa, G. Pourtois, V. V. Afanas'ev, and A. Stesmans, *Physica E* **56**, 416 (2014); E. Scalise, in *2D Materials for Nanoelectronics*, edited by M. Houssa, A. Dimoulas, and A. Molle (Taylor & Francis, London, 2016), p. 141.
- ⁵³T. Cheiwchanchamnangij and W. Lambrecht, *Phys. Rev. B* **85**, 205302 (2012).
- ⁵⁴D. A. Neamen, *Semiconductor Physics and Devices* (Irwin, Boston, 1992).