Thermal stability and temperature dependent electron spin resonance characteristics of the As acceptor in geological 2H-MoS₂

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Abstract

Electron spin resonance (ESR) results are presented on the thermal stability and temperature dependence of the ESR spectral characteristics of the As acceptor dopant (As substituting for S site) in geological 2H-MoS₂. Under sequential isochronal heating in H₂ (1.1 atm), the As dopant density is found to remain unaffected for anneal temperatures (T_{ans}) up to 525 °C, above which the density moderately decreases (~ 3 times) for $T_{\text{an}} \rightarrow \sim 840$ °C. In turn, vacuum annealing is seen to result in a gradual increase (2–3 times) of the As acceptor density for T_{an} increasing from 400 °C $\rightarrow \sim 840$ °C, pointing to a positive ‘regain’ of misconfigured As impurities in pristine geo-MoS₂. Finally, meticulous monitoring of the ESR signal intensity versus temperature at X-band confirms the previously inferred As acceptor activation energy of 0.7 ± 0.2 meV at K-band. The appropriateness of the latter ESR probing and analysis approach has been consolidated by application to the archetypal case of decoupled P donors in n-Si, resulting in an ESR-determined activation energy (42 ± 4 meV) well in agreement with the generally accepted one. In light of these findings, As is confirmed as a promising candidate for stable covalently bonded p-type doping of MoS₂.

Keywords: molybdenum disulfide, As acceptor, dopant activation energy, EPR, substitutional p-type doping, thermal stability of dopants

(Some figures may appear in colour only in the online journal)

1. Introduction

Propelled by the discovery of graphene [1], two dimensional (2D) transition metal dichalcogenides (TMDs) have emanated as promising candidates to revolutionize the current semiconductor technology as they could potentially replace conventional semiconductors in future nanoelectronic devices [2–8]. Among the comprehensive family of TMDs, molybdenite (MoS₂) has been widely studied for its outstanding properties: it is composed of layered stacks of hexagonal covalently bonded S–Mo–S unit sheets, forming an atomically thin, strong, and flexible layered semiconductor with an advantageous direct band gap of ~ 1.85 eV in monolayer form and an indirect band gap of ~ 1.3 eV in bulk form [2, 3]. Owing to its unique characteristics, MoS₂ is particularly well suited for incorporation in innovative integrated circuits and optoelectronic devices like e.g. photodiodes, light-emitting diodes, and flexible and transparent electronics [2, 3]. Additionally, the interlayer van der Waals bonding character of the

2D sheets potentially allows for multi-material stacking with other 2Ds that are characterized by different mechanical, electrical, and optical properties [9]. This novel approach would enable the creation of advanced heterostructure devices with no lattice mismatch issues and unprecedented functionalities.

While the potential of TMDs, and MoS₂ in particular, to be incorporated in a variety of future devices seems promising, the production of high quality large area layers still presents itself as a major challenge. Similar to other layered materials, pristine MoS₂ flakes can be obtained by micromechanical exfoliation, resulting in the current highest mobility MoS₂-based devices [4, 10, 11]. However, not

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different from other production methods like e.g. chemical vapor deposition (CVD), sulfurization and atomic layer deposition, exfoliated flakes suffer from the presence of impurities as well as native defects which hamper electronic transport properties. Therefore, a thorough understanding of the role of defects and impurities is of key importance for intended applications.

Evidently, besides reliable production, full exploitation of the unique properties of MoS₂ as atomically thin semiconductor material in novel devices requires reliable, well controlled doping, preferably achieved by stable covalent bonding of substitutional impurities. Yet, the current essential knowledge on dopant characteristics, including its nature, concentration, thermal stability and, crucially, corresponding energy level positioning within the MoS₂ band gap, is still limited.

Albeit with fluctuating awareness, electrical doping of MoS₂ has not been left unattended in the past. However, the interest in understanding and introducing controlled, stable doping of MoS₂—both theoretically and practically—has accelerated steadily over the recent years, obviously propelled by the endeavor after 2D applications (see, e.g. [12] for a brief synopsis and references therein). Both doping by intrinsic defects and (substitutional) impurities have been addressed.

As characterized, and mostly identified, by electron spin resonance (ESR)—the method of the current work—, the latter category includes Re (substituting for Mo) in 2D MoS₂, operating as a donor [13], as well as the acceptors Zr, Nb, As, and V in 3R-MoS₂ grown by chemical vapor transport [14, 15], and As [14, 16] in natural (geological) 2H-MoS₂ and N [12, 17, 18] in synthetic CVD-grown 2H-MoS₂. Also the Pb impurity, likely substituting for Mo and operating as acceptor, has been tentatively assigned by ESR [19]. Only recently, the thermal activation energy, E_a , of impurity dopants has been exclusively and atom-specifically assessed by ESR, reporting for 2H-MoS₂ the values E_a

$= 0.7 \pm 0.2$ meV and 45 ± 7 meV for As [16] and N [17], respectively, with a lower bound value, $E_a > 10$ meV, being

estimated for Pb [19].

The current work reports and expands on the identification by a multi-frequency ESR study of the As acceptor in geological 2H-polytype MoS₂, with the As impurities substituting for S sites. Careful monitoring of the ESR signal intensity over a broad temperature (T)-range previously revealed the As dopant as a very shallow acceptor with activation energy $E_a \approx 0.7$ meV [16].

Progressing on these findings, this work presents a detailed analysis of the thermal stability and reactivity of the As acceptor under heat treatment in H₂ and vacuum, including a comparison with the N acceptor in synthetic 2H-MoS₂ [12]. Additionally, the As acceptor's activation energy has been separately extracted from X-band ESR to verify the initial assessment based on K-band observations [16]. Finally, to consolidate the latter applied probing and interpretation approach, the activation energy of the P donor in n-Si is obtained from K-band ESR measurements and compared to the commonly accepted value of ~45 meV [20].

2. Experimental details

The material studied in this work is a commercially obtained [21] bulk geological MoS₂ crystal of 2H-polytype (hexagonal symmetry, two MoS₂ layers per repeat unit and Mo in trigonal prismatic coordination bonded to 6 S atoms). A thermoelectric test demonstrated the sample to be manifest p-type, as also evidenced by the observed As acceptor ESR spectra.

Thin (~0.2–0.4 mm) slices of ~2 × 8 mm² main area were cut from the parent MoS₂ crystal, with the c-axis along the main face normal n, appropriate for ESR study.

ESR observations were carried out over the T-range 1.5–40 K by means of standard continuous wave absorption X-band (~8.9 GHz) and K-band (~20.4 GHz) spectrometers. First derivative spectra were recorded using harmonic modulation ($B_m \cos(\omega_m t)$, with $\omega_m/2\pi \approx 100$ kHz) of the applied magnetic field B.

Essentially, both observational frequencies may be equally well applied for reliable analysis of the As ESR signal in all its aspects. However, K-band observations are here routinely performed because of the intrinsically higher sensitivity of this locally constructed spectrometer than the X-band one. The latter is involved in this work to independently verify key defect parameters, such as the acceptor activation energy, initially inferred from K-band work, or, in some cases, to facilitate optimal sample mounting in the cavity.

For each specific investigation of ESR signal intensity versus-temperature behavior, ESR observations were generally made either for B//c-axis or B ⊥ c-axis, with B uniformly (relative field inhomogeneity <1.5 × 10⁻⁶ over sample size) applied over the entire sample. As it is known the As acceptor ESR signal in MoS₂ to show profound g anisotropy (see, e.g. [15, 16]), this ensures measurement of

‘identical’ spectra (with respect to g) over the entire case study.

In aiming for accurate determination of defect (acceptor) densities—of prime interest here—and g values, use was made of two co-mounted isotropic marker signals (samples), i.e. Si:P [$g(4.3\text{ K}) = 1.998\,69 \pm 0.000\,02$; spin $S = 1/2$] [22] and LiF:Li ($g = 2.002\,293 \pm 0.000\,002$; $S = 1/2$) [23], both well calibrated in terms of absolute number of spin centers included and g value. Generally, both markers may in principle serve equally well for assisting in analysis of a studied ESR signal; preference of one before the other for use in a specific study just stems from considerations about ‘opportunistic’ spectroscopic adequacy, such as avoiding signal overlap (making use of difference in g value), line width considerations, etc. The defect density is derived from the ESR signal intensity, obtained as the double numerical integration of the detected $dP_{\mu r}/dB$ signal, where $P_{\mu r}$ is the reflected microwave power. Though not a major subject here, the calibrated g markers optimally allowed for accurate g value monitoring. In line with previous findings [16], the As ESR signal g value is observed to remain constant within experimental accuracy over the whole observational T -range covered, and no change is noticed as a function of anneal temperature either. In experimenting, attention was paid to

2
Semicond. Sci. Technol. 34 (2019) 035022 B Schoenaers et al
avoid spectral signal distortion through careful control of spectrometer settings, i.e. appropriately restricted magnitudes of B_m and incident microwave power P_{μ} (see, e.g. [24] for a general outline of the effects of (over)modulation and microwave saturation on the spectral appearance). In the current work, values were limited as: $B_m = 0.5\text{ G}$ (both X and K-band), $P_{\mu}(\text{X-band}) = 0.3\text{ }\mu\text{W}$, and $P_{\mu}(\text{K-band}) = 8\text{ nW}$ for $T = 10\text{ K}$ and $P_{\mu}(\text{K-band}) = 25\text{ nW}$ for $10\text{ K} < T < 40\text{ K}$.

As for the current geological MoS_2 material studied, the As dopant density in the as-received sample has been determined by ESR as $\sim 6 \times 10^{17}\text{ cm}^{-3}$, the value remaining unaltered after reference setting thermal treatment in vacuum ($\sim 400\text{ }^\circ\text{C}$). As outlined previously [16], the measurements have been carried out at sufficiently low T ($\sim 2\text{ K}$) where the As dopants reside in their electrically non-activated (i.e. ESRactive) state, thus ensuring assessment of the full As acceptor system.

3. Results and discussion

3.1. Dopant thermal stability

Aiming at a better understanding of the dopant stability and reactivity, the As acceptor has been subjected to two series of thermal treatments, one performed in H_2 (1.1 atm), the other in high vacuum ($< 7 \times 10^{-6}\text{ mbar}$). Isochronal thermal steps ($\sim 45\text{ min}$) were performed sequentially on two pieces of the

same sample, priorly subjected to a 'reference' setting treatment in vacuum ($\sim 400^\circ\text{C}$; $\sim 21\text{ h}$), referred to as the initial state. Thermal treatments were performed using a conventional resistively heated furnace system foreseen with a double-walled high-purity quartz insert, as described elsewhere [25].

The main purpose of the thermal treatment in H_2 is to investigate possible inactivation (passivation) of the acceptors through defect-H bond formation, inspired by the passivation behavior of some dopants in other semiconductors (see, e.g. [26]). Afterwards, the sample is subjected to subsequent anneals in vacuum in an attempt to get a better understanding of the reactivation (defect-H bond dissociation) of the acceptors (see, e.g. [27] and references therein). Concurrently, the extensive thermal treatment investigation also provides valuable insight into the overall structural thermal stability of the substitutional acceptor impurities.

Figure 1 shows the evolution of the As ESR signal intensity, which is proportional to the non-activated As acceptor density, over the various thermal treatments. Looking at the data corresponding to the vacuum thermal treatments, a first trend is revealed: starting from its reference value observed after heating in vacuum at an anneal temperature $T_{\text{an}} = \cdot 400^\circ\text{C}$, the signal intensity increases gradually for subsequent thermal steps T_{ans} up to 840°C likely tending to reach a plateau at a ~ 2.5 times higher value for $T_{\text{an}} = \cdot 700^\circ\text{C}$.

In studying a geological MoS_2 specimen, one may advance various interpretations for this effect. In a first view one may suggest it to result from structurally 'ill configured' As atoms moving to the 'proper' dopant position under thermal stimulus. Alternatively, it may concern a defect reactivation effect, e.g. defect-H bond breaking, or, perhaps better, defect 'decomplexation' in general: as exposed [6], geological MoS_2 is known to be besieged by a multitude of different impurities, some of which may tie up with As. Anyway, in both views, the general message is that the As impurity concentration actually present is higher than that corresponding to the initially observed As acceptor concentration, and additional As impurities can be regained for the proper acceptor doping bath by thermal treatment. As to the thermal treatment in H_2 , the As signal is seen to remain unaffected, within experimental accuracy, for heating up to $\sim 525^\circ\text{C}$, to then gradually be decreased by a factor of three at $T_{\text{an}} \approx \cdot 840^\circ\text{C}$. The latter behavior is in contrast with that of the N acceptor in synthetic MoS_2 [12] which experiences a drastic ESR intensity drop by an order of magnitude at $T_{\text{an}} \approx \cdot 500^\circ\text{C}$. Yet, for both acceptors, the intensity decrease can be tentatively ascribed to the direct passivation (inactivation) of the respective acceptors through defect-H bond (or defect-H complex) formation, similar to previous results for inactivation of point defects, such as, e.g. boron

acceptors in Si [26]. Notably, the apparent gradual intensity decrease of the As acceptor points to a significantly higher activation energy for passivation when compared to the N acceptor which experiences a more abrupt intensity drop in the T_{an} -range ~ 370 °C–500 °C [12].

Figure 1. Evolution of the As acceptor ESR signal intensity (K-band) as a function of isochronal heating in H_2 (blue squares) and vacuum (red circles). ESR measurements were carried out at $T \approx 4.2$ K for

$B \perp n$ using $B_m = 0.5$ G and $P_{\mu} = 25$ nW. The signal intensity increases gradually after sequential thermal treatments in vacuum and appears not affected in H_2 up to ~ 525 °C. The signal intensity decreases after thermal steps in H_2 by a factor of about three from ~ 525 °C to ~ 840 °C to be only partially recovered after a vacuum anneal at 840 °C (green diamond). The decrease of the signal intensity in H_2 is tentatively ascribed to passivation of the As acceptors by bonding to H. Error bars denote the uncertainty $[(\text{maximum value} - \text{minimum value})/2]$ for the set of data taken at a specific temperature. The dashed curves guide the eye.

Additionally, contrary to the case of the inactivated N acceptors that cannot be reactivated at temperatures up to $\sim 740^\circ\text{C}$ [12], (partial) reactivation of the As acceptor signal intensity by approximately a factor of two does occur at $T_{\text{an}} = 840^\circ\text{C}$ in vacuum (see figure 1). The latter would indicate that the activation energy for reactivation of the As acceptors is significantly higher than the corresponding activation energy ($E_{\text{act}} = 3.3\text{ eV}$) for the N acceptor estimated in previous work [12].

3.2. Temperature dependence

3.2.1. Dopant activation energy. Besides serving as an exclusive technique for atomic identification and thermal stability assessment of dopant impurities, ESR also provides the unique possibility to reliably determine the dopant-type specific activation energy through monitoring versus T the ESR signal intensity which is proportional to the concentration of non-activated acceptors. The acceptor activation energy, denoted as $E_a = E_A - E_V$ with E_A the acceptor energy level and E_V the valence band (VB) maximum, can then be obtained by interpreting the data using the proper mathematical expression (equation (1)) derived within the standard semi-classical solid state theory of band structure for well-defined conditions, as discussed before [16, 28].

For the current purpose, the As acceptor signal is monitored for B//c-axis using X-band ESR, figure 2 showing a representative spectrum ($g_{\text{eff}} = 2.027(1)$) observed at $T = 4.2\text{ K}$, together with the co-mounted LiF:Li marker signal ($g = 2.00229$). Figure 3 shows the attained normalized ESR intensity-versus- T behavior of the ^{75}As hyperfine (hf) quartet signal after proper correction for the admitted Curie-type susceptibility $\chi \propto 1/T$ -dependence of the spin system's specific magnetism [16]. As demonstrated by the dashed curve, i.e. plot of equation (1) for $E_a = 0.7\text{ meV}$, the data reliably confirm the previously obtained strong activation-driven signal intensity decay of the As acceptor at K-band, where from the latter data, the value $E_a = 0.7 \pm 0.2\text{ meV}$ had been inferred [16]. The data are interpreted (see dashed curve in figure 2) using the expression for the ratio of neutral, ESR-active, N_A^* , to total, N_A , acceptor densities derived from dopant occupation statistics [16, 28]

$$\frac{N_A^*}{N_A} = \frac{1}{1 + \exp\left(\frac{E_a}{kT}\right)}$$

$$\frac{1}{A} \exp\left(-\frac{E_A}{kT}\right)$$

with $K = \frac{4g_d N_A}{N_v} = \frac{4g_d N_A}{N_v} T^{-3/2} \equiv K_0 T^{-3/2}$ where

$N_v = \frac{2(2\pi m_v kT/h^2)^{3/2}}{2} \equiv N_{v0} T^{3/2}$ is the VB effective density of states, g_d represents the impurity level spin degeneracy factor inserted for bulk MoS₂ as $g_d = 2$ considering that there appears to be no band degeneracy at the top of the VB [28, 29], m_v is the hole effective mass, tabulated for MoS₂ as $m_v = 0.56m_0$ [29, 30] with m_0 the electron rest mass, k is Boltzmann's constant and h Planck's constant. The VB effective density of states is obtained as

$$2.02 \times 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2}.$$

Equation (1) represents the ideal case, valid for the conditions of a semiconductor absolutely dominated by one kind of dopant with negligible compensation or intrinsic excitation and non-degenerate doping. The current As dopant is present in a density that reliably meets the condition of nondegeneracy and presumably also that of negligible compensation, the As impurity being most likely by far the main type of dopant [31].

3.2.2. Model substantiation: the P donor in Si case. In further verifying the validity of the activation energy assessment

Figure 2. Typical derivative absorption X-band ESR spectrum of As acceptor impurities in bulk geological 2H-MoS₂ observed for $B//n$ at 4.2 K using incident microwave power $P_{\mu} \approx 0.3 \mu\text{W}$ and $B_m = 0.5$ G. The narrow signal at $g = 2.00229$ stems from the comounted LiF:Li marker sample.

Figure 3. T-dependence of the X-band ESR intensity (double integral of derivative absorption spectra; B//c-axis) of the ^{75}As hf ESR pattern originating from single decoupled As acceptors in geological 2H-MoS₂. The data, recorded over the T range 1.6–32 K, are normalized to the low T plateau value (T = 1.6 K) after correction for the admitted $\chi \propto 1/T$ -dependence. The dashed curve represents equation (1) plotted with $E_a = 0.7$ meV. The error bars represent the uncertainty within data sets.

4

Semicond. Sci. Technol. 34 (2019) 035022 B Schoenaers et al
 based on employing equation (1) to analyze the ESR dopant intensity versus T behaviour, the current interpretation approach has been independently tested on a sample taken from an n-type (100)Si wafer P-doped to a density of, as determined by ESR, $[P] = (1.0 \pm 0.1) \times 10^{17} \text{ cm}^{-3}$, well in agreement with the value $9 \times 10^{16} \text{ cm}^{-3}$ specified by the supplier on the basis of conductivity data. In illustrating the subject of study, figure 4 shows a typical X-band spectrum (T = 22.5 K) of isolated ^{31}P donors (substituting for Si) in c-Si, appearing as the well-known iso-shaped ~41 G split doublet, (see, e.g. [32]) together with the signal of the comounted

Si:P marker ($g \cdot = \cdot 1.9987$).

Similar to the As acceptor, the P donor most likely meets the same conditions required for the proper application of equation (1), i.e. non-degenerate doping dominated by one kind of dopant and negligible compensation. Figure 5 presents the temperature dependence of the normalized X-band ESR signal intensity corresponding to the ^{31}P hf doublet stemming from single decoupled P dopants in Si. Optimized fitting of equation (1) to the data shown in figure 5 results in $E_a = \cdot 42 \cdot \pm \cdot 4 \text{ meV}$, well in agreement with the commonly accepted value of $\sim 45 \text{ meV}$ [20], thus substantiating the interpretation model outlined in the previous paragraph.

3.2.3. As clusters. As described before [16], only 13% of the total As spectrum is found to be composed of the ^{75}As fourpeak hf structure, corresponding to dopants residing in the preferred 'isolated' doping state, while the major part of the spectrum (87%) has been attributed to exchange-coupled As acceptors denoted as 'cluster' formation. In the context of the process of the determination of the dopant E_a through ESR signal intensity monitoring, it may thus be valuable to closer verify the T-dependence of the latter part of the ESR spectrum.

Figure 6 shows a least-square linear fitting of the inverse signal intensity of the total As spectrum versus T, exposing a paramagnetic ($\chi \cdot \propto \cdot (T \cdot - \cdot T_c)^{-1}$) behavior with a close to zero

Curie–Weiss temperature $T_c = \cdot -1 \cdot \pm \cdot 1 \text{ K}$, similar to the results found for other dopants in Si [22, 33]. This clearly demonstrates the limited influence of the genuine intensity

Figure 4. Typical X-band ESR spectrum of single decoupled ^{31}P donors substituting for Si in n-type c-Si observed at 22.5 K. The dashed lines mark the ~ 41 G splitting of the well-known iso-shaped ^{31}P hf doublet. The central signal at $g \approx 1.9987$ stems from the comounted Si:P marker sample.

Figure 5. T-dependence of the K-band ESR intensity (double integral of derivative absorption spectra) of the isotropic ^{31}P hf doublet stemming from single decoupled P dopants in n-type c-Si. Optimized fitting of equation (1), represented by the dashed curve, results in an activation energy $E_a = 42 \pm 4 \text{ meV}$ which is in excellent agreement with the commonly accepted value of $\sim 45 \text{ meV}$, [20] providing confidence in the applied interpretation approach (see equation (1)). The error bars reflect the uncertainty within data sets.

Figure 6. T-dependence of the inverse X-band ESR intensity (double integral of derivative absorption spectra; $B \perp c$ -axis) of the total As spectrum. The dashed line represents a least-square linear fitting of the inverse signal intensity versus T demonstrating a paramagnetic ($\chi \propto (T - T_C)^{-1}$) behavior with a close to zero Curie–Weiss temperature $T_C = -1 \pm 1$ K. The error bars indicate the uncertainty reflected in the data sets.

5

Semicond. Sci. Technol. 34 (2019) 035022 B Schoenaers et al

decrease of the ^{75}As hf quartet on the total intensity, accentuating the importance of taking into account only the four-peak hf part of the total spectrum to reliably determine the acceptor activation energy corresponding to decoupled dopants; as known from ESR insight, such (primary) hf structure reflects electron-nuclear interaction at isolated impurities doping in the desired ‘ideal’ decoupled manner. Pertinently, we may add here that for the case of the above P-in-Si study, it is also the intensity of the hf component of the ^{31}P ESR signal (in this case, naturally only being composed of hf parts) that has been monitored versus T to correctly infer $E_a(\text{P})$.

Obviously, on statistical grounds, the chance for clustering will rise with increasing impurity content, the more so for systems out of equilibrium. Yet, while part of the relatively large fraction of As cluster formation may have been rendered by the encountered, rather high, concentration of As impurities, the bunching is likely more tied to the history and modalities (i.e. temperatures, ambient, dispersion, etc) of the sample formation over geological periods, beset with growth irregularity and inhomogeneity. In the latter view, it can thus not be excluded that, even in geo-MoS₂ of asincorporated significantly lower As impurity concentration, there may still be present a considerable fraction of As clustering. Deeper insight on this may be gained from a comparative ESR study on a set of synthetic MoS₂ specimen controllably doped by As to desired different concentrations.

4. Conclusions

In summary, the As acceptor emerges as a quite robust dopant of bulk geological MoS₂ as it sustains annealing in neutral ambient (vacuum) up to 840 °C. When subjected to sequential 'harsh' thermal treatments in H₂ up to this T, some decrease in As acceptor density is observed, but not nearly as drastic as for the N acceptor in synthetic MoS₂. Moreover, the As acceptor signal intensity could only be partially recovered at 840 °C in vacuum.

As to its dopant properties, the previously obtained As acceptor activation energy of 0.7 ± 0.2 meV at K-band, corresponding to decoupled dopants, has been firmly consolidated by X-band observations. The total As signal on the other hand exhibits a close to zero Curie–Weiss temperature with no appreciable influence of dopant activation. The validity of the applied interpretation approach is firmly consolidated by a first activation energy assessment by ESR of P dopants in n-Si, demonstrating an excellent agreement with the commonly accepted activation energy for decoupled P donors in Si.

In general, the current work firmly establishes As as utmost appropriate for covalently bonded p-type doping of MoS₂ both in terms of its excellent thermal stability and appropriate activation energy.

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