Diamond detectors for high-temperature transactinide chemistry experiments

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Abstract

Here, we present the fabrication details and functional tests of diamond-based α -spectroscopic sensors, dedicated for high-temperature experiments, targeting the chemistry of transactinide elements. Direct heating studies with this sensor material, revealed a current upper temperature threshold for a safe α -spectroscopic operation of $T_{det} = 453$ K. Up to this temperature, the diamond sensor could be operated in a stable manner over long time periods of the order of days. A satisfying resolution of ≈ 50 keV FWHM was maintained throughout all conducted measurements. However, exceeding the mentioned temperature limit led to a pronounced spectroscopic degradation in the range of 453 – 473 K, thereby preventing any further α -spectroscopic application. These findings are in full agreement with available literature data. The presented detector development generally enables the chemical investigation of more short-lived and less volatile transactinide elements and their compounds, yet unreachable with the currently employed silicon-based solid state sensors. In a second part, the design, construction, and α -spectroscopic performance of a 4-segmented diamond detector, dedicated and used for transactinide element research, is given as an application example.

Keywords: Diamond, detector, alpha-spectroscopy, high-temperature, transactinides, vacuum chromatography

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1. Introduction

The chemical properties of transactinide elements with atomic numbers $Z \geq 104$ (also referred to as superheavy elements, SHEs) are investigated at the one-atom-at-a-time level. These low amounts result as a consequence of the extremely low production rates. This demanding task of handling single atoms of usually very short-lived radionuclides requires highest efficiencies and shortest processing times.

Chemical studies with SHEs probe the fundamental ordering schemes of the periodic table at its very limits. With increasing nuclear charge, electrons are progressively subjected to relativistic effects [1, 2]. These effects influence the chemical behavior of all elements and roughly scale with Z^2 [3]. Thus, despite moderate effects on the chemical behavior of the lighter elements, strongest impacts can be expected for the heaviest ones in the region $Z \geq 104$. Therefore, chemical studies with SHEs contribute to the completion of modern atomic structure theory and to the accurate description of the underlying relativistic effects by providing experimental data for the purpose of qualification of the proposed models [4].

Gas-phase chromatography systems are successfully applied for the fast chemical characterization of SHEs with half-lives of $t_{1/2} \geq 1$ s. State-of-the-art devices such as the Cryo On-Line Detector (COLD) [5] and the Cryo-Online Multidetector for Physics And Chemistry of Transactinides (COMPACT) [6] consist of arrays of consecutive detector pairs [7]. The two detectors of such a pair are mounted in a sandwich-like geometry, thereby forming an open rectangular channel. By applying a temperature gradient from around 313 K down to approximately 90 K, such a channel acts as a chromatography column for the spatial thermochromatographic separation of different chemical species. These are then identified by means of detecting the emitted α -particles and/or spontaneous fission fragments of the mother nuclide itself as well as of its decay products. The elements or compounds are spatially separated along this channel according to their adsorption interaction with the coverage of the detector surface, serving as the stationary phase. These dedicated systems together with sophisticated data acquisition electronics enable time-correlated event-by-event α -decay and spontaneous fission spectroscopy and thus, allow for unprecedented identification sensitivities down to single atoms per week. Such setups are used to address the characteristics of the adsorption interaction of fairly volatile elements or their compounds with standard adsorption enthalpies from $-\Delta H_{ads}^\circ \approx 60 \text{ kJ}\cdot\text{mol}^{-1}$

Figure 1: Thermochromatographic deposition pattern (i.e., internal chromatogram) of ^{185}Hg (plain) and ^{219}Rn (hatched) within the COLD array on gold (until detector ≈ 19) and ice (from detector ≈ 19 onwards). The corresponding Monte Carlo simulations are shown (short dashed/dotted lines) together with the temperature gradient (dashed line, right-hand scale). The given temperature threshold T_{max} indicates the maximum operation temperature of a common Si-PIN diode α -detector. Figure adapted from [8].

to $15 \text{ kJ} \cdot \text{mol}^{-1}$ (see Fig. 1). However, species with higher adsorption enthalpies, i.e., less volatile species, are currently not assessable by means of these setups. This limitation arises from the upper temperature threshold of the utilized silicon-based solid state detectors. When exceeding $\approx 313 \text{ K}$, thermal excitation of the semiconductor material sets in. The thereby massively enhanced intrinsic charge carrier density prevents then any further spectroscopic application. Thus, an alternative solid state sensor material is needed.

Diamond has an almost five times larger band gap of 5.4 eV compared to the one of silicon, i.e., 1.12 eV [9]. Therefore, the intrinsic charge carrier density of a pure mono-crystalline diamond sensor will only reach the same level as the one found in a Si-based sample, operated at room temperature, at around $\approx 1300 \text{ K}$ [10]. Thus, a comparable performance of both devices is expected in the stated temperature regimes, which makes diamond well suited for applications of nuclear spectroscopy in high-temperature environments.

82 So far, unfortunately, various difficulties, generally related to the demanding
83 task of artificial diamond synthesis of ultra-pure single crystals, hampers to
84 fully exploit this property.

85 Observations related to the applicability of diamond as a radiation sensor
86 were already made in 1923 in the course of work done on the material's pho-
87 toconductivity [11]. First radiation measurements succeeded using selected
88 natural diamond samples [12, 13, 14, 15]. These studies were successfully con-
89 tinued with synthetic diamonds, grown by the high pressure high temperature
90 method (HPHT) [16]. However, it was not until major advances had been
91 made related to the chemical vapor deposition (CVD) production process
92 before the diamond-based detector technology became more readily avail-
93 able [17, 18]. Regarding latest production advances such as the reduction of
94 residual impurities (i.e., nitrogen and boron), available single-crystal sample
95 sizes, and favorable price developments, electronic grade single-crystal CVD
96 (escCVD) diamond [19] has been increasingly applied in nuclear spectrom-
97 etry ever since. Detectors made from diamond sensors finally reached and
98 almost surpassed the performance level of the widely applied silicon-based
99 solid state detectors [20, 21]. The particular task of operating diamond de-
100 tectors at high temperatures was explored early on using selected natural
101 diamond samples [15] and with diamonds obtained from the HPHT method
102 [22]. More recently, these studies have been pursued with the escCVD dia-
103 mond material [23, 24]. However, none of these studies was entirely able to
104 surpass an upper temperature limit for α -spectroscopy of 473 K. Consistently
105 throughout all conducted measurements, reaching this temperature thresh-
106 old led to a severely deteriorated spectroscopic behavior and a significantly
107 decreased charge carrier collection efficiency.

108 Here, we present the production of escCVD diamond-based sensors and
109 their application in high-temperature environments. Thereby we provide a
110 way of substantially exceeding the faced temperature limitation of current
111 gas-phase SHE chemistry experiments. The detector fabrication from the
112 bare as-grown CVD material to a fully operational unit is outlined. We re-
113 port on the temperature dependent α -spectroscopic performance of a single-
114 crystal, electronic grade CVD diamond sensor using a Joule heating method.
115 In the second part, an advancement in the form of a 4-segmented diamond de-
116 tector is presented. Its associated spectroscopic behavior is briefly addressed.
117 This detector has been successfully applied in the first-ever investigation of
118 the adsorption interaction of elemental thallium on quartz [25].

119 2. Accessing less volatile species

120 The investigation of less volatile elements and their compounds generally
 121 requires higher stationary surface temperatures. This was demonstrated, for
 122 example, during the investigations of halide and oxyhalide species of super-
 123 heavy transition metals [26]. However, a direct measurement of the deposited
 124 species was impossible due to the limitations given by silicon as a sensor ma-
 125 terial. Hence, an aerosol gas-jet transport was required to connect the high-
 126 temperature gas chromatography setup with the detection system [27]. In or-
 127 der to surpass the range of accessible adsorption enthalpies of modern on-line
 128 gas-phase chromatography experiments, stationary surface temperatures of
 129 $T > 313$ K need to be reached (Fig. 1 & 2). Consequently, such temperatures
 130 lead to higher directly applied heat loads and higher UV/vis/IR-radiation
 131 loads for the sensor material, while being placed as an integral detector in a
 132 thermochromatography setup, as described above, or in the form of an escape
 133 detector in an isothermal gas chromatography experiment [25].

134 The investigation of the elemental state of SHEs with $Z > 112$ is of
 135 particular interest. Thermochemical predictions based on relativistic density
 136 functional theory [28, 29, 30, 31, 32] render all $7p$ -elements as fairly volatile
 137 species. Nevertheless, addressing the chemical properties of these elements
 138 challenges a gas chromatographic system in a broad temperature range of
 139 roughly 100 – 1000 K. Thus, this clearly demonstrates the necessity of new
 140 detection techniques for future SHE chemistry experiments.

141 The temperature requirements for a set of standard adsorption enthalpies
 142 of element E113 (i.e., $^{284}113$, assuming $t_{1/2} = 1$ s) on quartz was mod-
 143 eled for an isothermal vacuum chromatography experiment (Fig. 2). For
 144 this purpose, a Monte Carlo simulation approach was used, based on a mi-
 145 croscopic kinetic description of the transport process and the adsorption
 146 interaction [33, 34, 35, 25]. The average retention time as a function of
 147 the isothermal stationary surface temperature and the adsorption enthalpy
 148 were obtained from simulations of a 100 mm long quartz column with an
 149 inner diameter of 2 mm. The standard adsorption enthalpy at zero sur-
 150 face coverage for the given physicochemical system is expected in the range
 151 of $-\Delta H_{ads}^{\text{SiO}_2} \approx 60 - 100 \text{ kJ} \cdot \text{mol}^{-1}$ [28] - a domain yet unreachable with
 152 silicon-based solid state detectors but addressable using diamond-based sen-
 153 sors (Fig. 2). Note here, that a fixed relation exists between the yield, the
 154 retention time, and the half-life. Hence, in an isothermal chromatography
 155 experiment, a 50% throughput yield results if the retention time equals the

Figure 2: Retention times t_{ret} as a function of the isothermal column temperature (stationary surface) and the adsorption enthalpy $-\Delta H_{ads}^{\text{SiO}_2(284113)}$ calculated using a Monte Carlo simulation approach. The current upper temperature limits are indicated (dashed lines) for the two applicable detector materials, i.e., silicon and diamond (the arrow indicates the theoretically attainable temperature range for diamond sensors). The 1 s retention time line (dashed-dotted line) and the area for a retention time interval of 3–28 h (horizontally hatched) are highlighted, approximately corresponding to the current experimental limit in terms of half-life.

half-life of the investigated radioactive species. The range of maximum, experimentally assessable retention times, or in other words the longest addressable half-lives, for any gas-phase chemistry experiment, including vacuum chromatography, is of the order of 28 h and has been marked in Fig. 2 (horizontally hatched area).

3. Sensor fabrication

All herein presented diamond sensors are exclusively based on electronic grade, single-crystal CVD diamond (escCVD; $4.5 \times 4.5 \times 0.5$ mm, part. no. 145-500-0390, *Element Six Ltd.*) [19]. Hydrogen, as the dominating species during the CVD production process, leads to a hydrogen-terminated diamond surface. As shown by [36, 37], such surfaces exhibit a p-type surface conduction in combination with atmospheric adsorbents, but are supposed to be highly insulating in ultra high vacuum, i.e., in the absence of these adsorbents. Hence, surface conduction may lead to an electrical short circuit across the sample surface between the two electrodes of a single sensor unit in parallel-plate geometry. This has to be prevented by all means in order to ensure a proper detector operation under all experimental conditions, which is why a highly resistive oxygen-terminated surface is typically chosen. Such a one can be achieved through wet etchings with strong oxidants. Thus, the as-delivered material with its hydrogen-terminated surface and remaining graphite phases (e.g., from post-growth laser cutting) was cleaned and oxidized using the following procedure. First, the sample was submerged under reflux in a bath (3:1) of H_2SO_4 (95 – 97%, Baker Analyzed® Reagent, *J. T. Baker*) and HNO_3 (65%, AnalaR Normapur, *VWR Chemicals*) at $\approx 200^\circ\text{C}$ for about 1 h. After being rinsed with ultra-pure water, it was once more treated for another half-hour in a bath (1:1) of HCl ($\sim 36\%$, Analytical reagent grade, *Fisher Scientific*) and H_2O_2 (30%, AnalaR Normapur, *VWR Chemicals*) at $\approx 70^\circ\text{C}$. The diamond plate was then sonicated for about an hour in ultra-pure water at 60°C prior to the metallization.

The cleaned escCVD diamond sample was then mounted in a dedicated aluminum frame, acting on one side as a shadow-mask, while leaving the other side fully exposed (Fig. 3). Up to four plates are held in position by spring pins. These are introduced and fixed sideways, thereby pushing the plates toward the cross-feature in the middle. Prior to the electrode deposition, the mask with the mounted sample(s) was passed through a final

Figure 3: The shadow mask front side for the metallization of up to four standard diamond plates ($4.5 \times 4.5 \times 0.5$ mm) with **1** the smaller frame on the back side for a partial surface coverage of the diamond plate (3.5×3.5 mm), **2** the indentation for the plates leaving the front side of the diamond plate fully exposed (metallization to the very edges), **3** the spring pins for holding the diamond plates in position, **4** a screw and **5** the spring pin fixation block.

192 cleaning stage in an UVO cleaner for 15 minutes (Model 42, *Jelight Company*
 193 *Inc.*). This process ensures nearly atomically clean surfaces and finalizes the
 194 oxygen-termination on the diamond surface itself. The sample holder was
 195 then immediately transferred and mounted inside a thermal evaporation sta-
 196 tion (UNIVEX 450, *Leybold Vacuum*) in order to diminish surface contami-
 197 nation. Both sides of the diamond plate were metalized first with a ≈ 10 nm
 198 flash of chromium followed by a ≈ 100 nm thick gold layer.

199 4. α -Spectroscopy at high temperatures

200 The high-temperature α -spectroscopic operation of an escCVD diamond
 201 sensor was tested up to 473 K in terms of associated quality parameters (i.e.,
 202 peak shift, spectroscopic resolution, and count rate) as well as their long
 203 term stability. A reliable performance over longer periods is a prerequisite
 204 for detectors in SHE chemistry experiments (see Sec. 5) and it was therefore
 205 addressed in the course of these studies. For this purpose, a dedicated heating
 206 setup was designed and developed (Fig. 4).

207 4.1. Experimental details

208 A 4.5×4.5 mm large and $500 \mu\text{m}$ thick escCVD diamond sensor plate [19]
 209 was prepared as described above (Sec. 3). The fully functional sensor unit

210 was then directly placed in an indentation with the size of the plate's dimen-
 211 sions, embedded on a copper block. This block was resistively heated by a
 212 high-power AC-driven heating cartridge ($P = 100$ W at 230 V, $d = 6.5$ mm,
 213 $l = 40$ mm), having an upper temperature operation limit of 1023 K. The
 214 temperature was regulated with respect to a type K thermocouple, inserted
 215 sideways just underneath the sensor position. During all experiments the
 216 temperature of the entire detector heating assembly was maintained within
 217 ± 1 K at the respective set point. The otherwise electrically insulated block
 218 mount was carefully grounded over a spring pin. The back electrode of the
 219 diamond detector was in direct electrical contact with the copper block sur-
 220 face and thus on ground potential. Meanwhile, the fully metallized front side
 221 was used for the bias-application of $+0.6$ V/ $\mu\text{m} \cdot 500 \mu\text{m} = 300$ V and for
 222 the signal extraction (i.e., operating in the hole drift mode ensures compara-
 223 bility to other studies). The hereto applied second spring pin served at the
 224 same time for holding the diamond detector tightly in position. Both of these
 225 spring pins were fixed and held in place by means of an electrically insulating
 226 MACOR[®] support structure (machinable glass ceramic, $T_{max} = 1073$ K).
 227 All parts of the whole heating structure were carefully chosen in order to
 228 endure a temperature range up to 1023 K (i.e., the limit of the heating car-
 229 tridge). Every conducted α -spectroscopic measurement was performed in
 230 vacuum at $p_{exp} < 1 \cdot 10^{-3}$ mbar. A reference 3-radionuclide α -source (main
 231 α -lines: ^{239}Pu [$E_\alpha = 5156.59(14)$ keV], ^{241}Am [$E_\alpha = 5485.56(12)$ keV], and
 232 ^{244}Cm [$E_\alpha = 5804.82(5)$ keV] [38, 39, 40]) was mounted in front of the as-
 233 sembly, facing the radiation sensor in ≈ 20 mm distance. The signal-readout
 234 and -processing was done using a customized version of the CIVIDEC Cx
 235 spectroscopy shaping amplifier [41] with a Gaussian pulse shaping time of
 236 $1 \mu\text{s}$ (rise time = 190 ns, gain = $10.9 \text{ mV} \cdot \text{fC}^{-1}$). The high gain and the
 237 adequate pulse shape of this amplifier type allowed for a direct coupling to
 238 an 8192 channel ADC/MCA readout system (Tukan8k, *Narodowe Centrum*
 239 *Badan Jadrowych*). All measurement electronics were connected from the
 240 outside of the vacuum housing.

241 4.2. Experimental results

242 All measurements of the reference source were recorded within an acqui-
 243 sition live time of $t_{live} = 1800$ s. The experimental assembly was heated up
 244 from room temperature to 373 K followed by consecutive steps of 20 K up
 245 to 473 K. From the obtained spectra the peak shift, the detector resolution,
 246 and the recorded count rate were extracted and summarized as functions of

Figure 4: The diamond detector heating setup with **1** the escCVD diamond sensor plate, **2** the heated copper block, **3** the high-power heating cartridge, **4** the type K thermocouple (pushed underneath the radiation sensor), **5** the spring pins for the electrical contacting, and **6** the MACOR[®] support structure. Kapton[®] insulated wires were crimped to the top ends of the spring pins to ensure a safe high-temperature operation.

247 temperature (Fig. 5, 6, and 7). Apart from the temperature adjustments, all
 248 measurements were conducted under exactly the same experimental condi-
 249 tions without any changes to the setup within the vacuum chamber.

250 With increasing temperature a distinct but otherwise stable peak shift
 251 toward higher channel numbers was observed, whereas the resolution ($\approx 1\%$
 252 for ^{239}Pu at room temperature, i.e., ≈ 50 keV FWHM) as well as the overall
 253 count rate remained at the same level within the uncertainty limits up to
 254 a temperature of 453 K (Fig. 5 & 7). The α -spectroscopic performance
 255 changed drastically between $T_{det} \approx 453 - 473$ K. Within this range, the
 256 spectroscopic resolution progressively worsens, whereas above $T_{det} = 473$ K
 257 this trend is further enhanced until the count rate in the region of interest
 258 collapses almost entirely. Accompanying these effects is an increasing noise
 259 level, apparent from an enlarged amount of low energetic events at small
 260 channel numbers.

261 All of these characteristics were fully reproducible within hours of mea-
 262 surement and applying a temperature cycle to the detector unit. This has
 263 been proven with three consecutive measurements (Fig. 6). The first one
 264 was recorded after the sensor had reached its final operation temperature of
 265 $T_{det} = 453$ K. Following this measurement, a full spectroscopic degradation

Figure 5: α -Spectra (scatter plots) of the reference source (^{239}Pu , ^{241}Am , and ^{244}Cm) and their fits (line plots) recorded at different temperatures but otherwise identical conditions. Normal operation without deterioration of the spectroscopic behavior was observed up to $T_{det} = 453$ K before a sudden change occurred above this threshold temperature toward $T_{det} = 473$ K.

Figure 6: Three α -spectra of the reference source (^{239}Pu , ^{241}Am , and ^{244}Cm) at an operation temperature of $T_{det} = 453$ K, each one recorded for $t_{live} = 1800$ s. The initial measurement (line) is shown with a second one after ≈ 19 h (circles), and a final measurement after ≈ 41 h (crosses), with periods applied in between during which the sensor temperature was increased to $T_{det} = 473$ K; for more details, see text.

266 was provoked (see Fig. 5) by heating the detector unit to $T_{det} = 473$ K. Sub-
 267 sequently, the sensor temperature was lowered down to $T_{det} = 433$ K, i.e.,
 268 into the stable α -spectroscopic operation regime. After having maintained
 269 this temperature level for ≈ 19 h, the sensor was once again brought up to
 270 $T_{det} = 453$ K for a second measurement. The third and last measurement was
 271 finally recorded additional ≈ 22 h later, after the sensor had been kept at the
 272 same temperature (i.e., $T_{det} = 453$ K), but in an unbiased state. Besides fully
 273 reproducing the general spectroscopic characteristics (Fig. 7), these mea-
 274 surements likewise prove the reversibility of the spectroscopic degradation
 275 at $T_{det} \approx 473$ K. After having returned to the apparently safe temperature
 276 range of $T_{det} \leq 453$ K, the sensor performance fully recovered.

277 4.3. Discussion

278 The obtained results in terms of an upper α -spectroscopic operation limit
 279 for a diamond sensor confirm early findings by F. Nava et al. [15] as well as
 280 the ones obtained by the group of Y. Tanimura [22], using selected natural
 281 diamond samples or artificial diamonds synthesized by the HPHT method,
 282 respectively. Likewise, the more recent observations by M. Angelone et al.
 283 [23] experienced the same limitations approaching 473 K. During these ex-
 284 periments, an escCVD diamond [19] as part of a commercial product from
 285 *Diamond Detector Ltd.* was tested together with a self-synthesized CVD
 286 diamond. Whereas the latter reached an upper temperature limit of ap-
 287 proximately 433 K, the commercially obtained sample could be operated at
 288 somewhat higher maximum temperatures of ≈ 453 K. This coincides exactly
 289 with the threshold found in this work. A very new study [24] encountered the
 290 overall same limitation for two out of three diamond detectors and seemingly
 291 pushed the operation limit further up to temperatures ≤ 573 K with a third
 292 sample. However, this was only possible by collecting electrons (i.e., hole
 293 drift mode) whereas the hole collection could not be recorded.

294 The charge carrier lifetimes in semiconductor devices strongly depend on
 295 the concentrations and cross sections of so-called deep levels, acting as trap-
 296 ping and recombination centers. For the case of mono-crystalline diamond,
 297 nitrogen impurities are the main constituent responsible for such deep levels.
 298 As it seems, experimentally observed deep centers in the forbidden gap with
 299 activation energies of ≈ 1 eV at large enough concentrations might be held
 300 accountable for the before mentioned temperature limitations of diamond-
 301 based sensors [42]. Depending on the charge carrier density, these energy lev-
 302 els can act as well as thermally triggered generation centers [22]. As shown

by T. R. Garcia and co-workers for SiC-based detectors, thermally stimulated dark currents up until $\approx 10 \mu\text{A} \cdot \text{cm}^{-2}$ do not lead to a measurable increase of the FWHM in an α -spectrum [43]. Below this current threshold, the resolution is determined by other, more dominating, noise effects, such as those originating from the used measurement electronics, rather than by the nature of the sensor itself.

The peak shift toward higher channels with increasing temperature (Fig. 5 & 7) is attributed to a slightly more efficient charge collection as seen in [22, 23] and as suggested by simulations of polycrystalline samples [44]. Thermal excitation from shallow trapping centers may lead to a faster release of trapped charge carriers and thus to an improved charge carrier collection efficiency [22, 45, 46]. In contrast to observations by [15, 22] no change occurred within the error limits concerning the resolution (middle section in Fig. 7) as well as the count rate (bottom panel in Fig. 7; integration ranges of ADC channels: 750 – 800 for ^{239}Pu , 800 – 850 for ^{241}Am , and 850 – 900 for ^{244}Cm , see Fig. 6). This holds even for long measurement times and intermediate temperature changes (Fig. 6). The slightly improving peak resolution with increasing temperature in case of the atmospheric α -spectroscopic measurements conducted by [23], might be partially ascribed to air density changes in the gap between the source and the heated detector assembly rather than to intrinsic effects within the solid state sensor itself. Note here, the overall more fluctuating trends for ^{244}Cm , which result from the rather low statistics compared to the other two radionuclides (Fig. 7).

Including this work, five independent studies have tested diamond samples of different origin and employed various metallizations for the electrical contacting [15, 22, 23, 24]. So far with one exception [24], an overall upper temperature limit of $T_{det} \approx 473 \text{ K}$ was consistently observed. As presented here, this temperature effect on the α -spectroscopic performance was fully reproducible, thereby excluding irreversible chemical processes related to the deposited electrodes and the underlying diamond material. The evolving large low-energy tailing when exceeding the critical thermal threshold, in combination with maintaining a steep high energy edge (affected by noise contributions), possibly occurs as a consequence of an enhanced charge carrier recombination. Meanwhile, the slight peak shift back to lower channel numbers might be ascribed to trapping-induced field distortions inside the sensor (see α -spectrum measured at the highest temperature, Fig. 5).

Thus summarizing, these facts, regarding the upper bound for a safe α -spectroscopic operation, seem to indicate intrinsic effects within the diamond

Figure 7: Summary of the three evaluated α -spectroscopic quality parameters, namely the peak shift (upper panel; deviation in permille from the peak position at room temperature), the resolution (middle panel), and the count rate (bottom panel) as functions of the temperature (68% confidence intervals are indicated). These properties were derived for all three lines of the reference α -source, i.e., for ^{239}Pu , ^{241}Am , and ^{244}Cm . Note the three different scales for the count rate individually applying to one of the three progressions (style-coded).

bulk itself. Charge generating deep energy levels in the forbidden band gap [42] may gain momentum as recombination or trapping centers upon thermal activation and the temporary charge density spikes, induced by penetrating α -particles [22]. Unfortunately, dark current measurements could not yet been pursued in the course of this work, but are in preparation. As shown before, e.g., by M. Angelone and co-workers [23] or as seen in [22, 24], the leakage current grows dissimilarly fast with increasing temperature. This may lead to tripping over the above mentioned critical threshold of $\approx 10 \mu\text{A} \cdot \text{cm}^{-2}$ [43] and thus, might serve as an additional explanation for the made observations.

5. First chemistry experiments

A 4-fold diamond detector was successfully used in a first-ever on-line isothermal vacuum chromatography experiment, targeting the adsorption enthalpy of elemental thallium on quartz [25].

5.1. Detector design

Four fully prepared diamond sensors (see Sec. 3) were glued together with four modified ceramic leadless chip carriers (CLCC, part. no. IRK28F1-247AAW, *NTK Technical Ceramics*) onto a custom-made printed circuit board (PCB; see Fig. 8) using an electrically conductive silver epoxy (EPO-TEK® H20S, *Epoxy Technology, Inc.*; curing time of 1 h at 150°C). The fully metalized front sides of all four sensor plates were interconnected using aluminum wire bonding and put on ground potential. Meanwhile, the back-electrodes were used for the single-channel HV-application and signal extraction. A considerable noise reduction can be achieved through a Faraday cage-like arrangement [47], which can be established by means of a sandwich structure with grounded metal masks on both sides of the sensor assembly (Fig. 8). This shielding needs to be designed in a way to cover up the entire PCB area of the detector with a single square hole in the middle of the top shielding for the exposure of the sensor assembly. Such a detector design allows measurements at highly reduced noise levels, presumably depleting RF frequencies up to 2 GHz [47].

5.2. α -Spectroscopic performance

Each diamond sensor was read out separately using each the customized version of the CIVIDEC Cx spectroscopy shaping amplifier [41] (see Sec. 4.1).

Figure 8: Exploded view of the detector assembly with **1** a diamond detector plate (fully metallized front side), **2** a cut and ground CLCC **3** the PCB front face at ground potential, **4** a signal extraction pad for the backside contacting of the rear diamond electrode, **5** the PCB, and **6** a LEMO00 plug for the signal read-out.

375 A positive bias of $+0.6 \text{ V}/\mu\text{m} \cdot 500 \mu\text{m} = 300 \text{ V}$ was applied to the back elec-
 376 trode (i.e., the sensor was operated in the electron drift mode), serving at the
 377 same time as signal read-out site. Four 200 mm long LEMO00-terminated
 378 50Ω cables were used to connect the 4-fold diamond detector to the am-
 379 plifier inputs on the outside of the vacuum chamber. An energy resolution
 380 (FWHM) of $\approx 1\%$ for ^{239}Pu ($\approx 50 \text{ keV}$) was achieved for all four sensor units,
 381 rendering this measurement setup ready for being used in experiments with
 382 transactinide elements (Fig. 9).

383 5.3. Chemistry experiment

384 During the chemical investigation of the adsorption behavior of thallium
 385 on quartz [25], the 4-fold sensor assembly was placed and operated in close
 386 proximity of an isothermal chromatography column exit (i.e., 5 mm between
 387 the hot oven end and the active area of the detector), which reached temper-
 388 atures of $\approx 1000 \text{ K}$. Due to the apparent high IR-radiation load and based
 389 on the above derived temperature limitation of $T_{det} \approx 453 \text{ K}$ (see Sec. 4),
 390 the detector was water-cooled from the back. The employed copper cool-
 391 ing block simultaneously served as the grounded back shielding of the before

Figure 9: Sample spectrum of the reference α -source (^{239}Pu , ^{241}Am , and ^{244}Cm) recorded at room temperature and $p_{exp} < 1 \cdot 10^{-3}$ mbar with a single diamond sensor for $t_{live} = 10$ h (source-to-detector distance: ≈ 20 mm). The dashed line corresponds to a superimposed peak-shape fit taking into account all α -lines having an intensity of $\geq 1\%$.

Figure 10: Final detector assembly as used in [25]. The Faraday cage-like structure was achieved through a sandwich assembly with **1** the 4-fold diamond sensor assembly in the middle, and **2** the front shield (with a square hole in the middle for the detector exposure), being electrically connected to **3** the grounded and water-cooled copper block in the back.

mentioned Faraday cage-like setup (Fig. 10). The detector assembly as seen in Fig. 8 was then covered from the top with an additional copper mask. This top cover had a central square hole for the detector exposure and was electrically connected to the grounded cooling block in the back. This structure efficiently shielded all underlying signal pads on the PCB board of the sensor assembly and helped establishing a reduced electrical noise level.

The high oven temperature leads to intense IR/vis/UV-loads incident on the detector. Without cooling, the sensor assembly reached a temperature of $T_{det} > 473$ K. However, the applied water-cooling ensured a safe operation temperature of $T_{det} \leq 453$ K and enabled a stable α -spectroscopic performance lasting for days. For further details see [25].

6. Conclusion

α -Spectroscopy studies at high temperatures using an escCVD diamond sensor revealed a constant and reproducible behavior over long measurement times up to $T_{det} = 453$ K. In accordance with available literature, the spectroscopic performance rapidly degraded when exceeding this operation temperature while closing in on ≈ 473 K. Ultimately, the count rate became largely suppressed in the region of interest after having surpassed this thermal threshold.

This sensor development extends the available temperature range for

thermochromatographic applications in future gas-phase chemistry studies of SHEs up to the stated temperature. Such an increase in temperature of the stationary surface translates into an upper adsorption enthalpy limit of approximately $-\Delta H_{ads}^{\text{SiO}_2} \leq 100 \text{ kJ} \cdot \text{mol}^{-1}$ for a short-lived species in a vacuum chromatography experiment. This extends the assessable region of future adsorption chromatography experiments considerably compared to what is currently possible with state-of-the-art Si-based detector setups.

Furthermore, a 4-fold diamond detector was successfully designed, constructed, tested and finally employed over periods of days as an escape detector in an on-line isothermal vacuum chromatography experiment. Intense IR/vis/UV-loads, emitted from the high-temperature end of a chromatography oven ($\approx 1000 \text{ K}$) in a few millimeters distance, did not affect the spectroscopic behavior. The detector revealed a satisfying α -spectroscopic performance in case of all four singly read-out channels, each of them featuring a peak-resolution of $\approx 1\%$ for ^{239}Pu at room temperature (i.e., $\approx 50 \text{ keV}$ FWHM).

The overall experienced temperature limit of a diamond sensor is by far below of what is theoretically possible in terms of the expected intrinsic charge carrier densities in dependence of the temperature. Thus, further studies aim to overcome even this threshold.

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