Growth and characterization of Arsenic doped CdTe single crystals grown by Cd-solvent traveling-heater method

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Abstract

We report the growth of *p*-type As-doped, Cd-rich CdTe single crystals using metallic Cd as the solvent in the traveling-heater method. We investigate the growth process from Cd solution in terms of the solid-liquid interface shape and the effects of As incorporation on *p*-type doping. The resulting CdTe crystals have Cd-rich composition which enhances *p*-type doping. The As doping efficacy was measured for As concentrations by the combination of inductively coupled plasma mass spectrometry, capacitance-voltage measurements. The *p*-type doping concentration varied from 6×10^{15} to $8 \times 10^{16} \text{ cm}^{-3}$ with increasing As concentration, with an apparent doping limit just below 10^{17} cm^{-3} .

Keywords : A1. Growth interface, A2. Growth from solutions, A2. THM, B2 CdTe.

23 **Introduction**

24 Cadmium telluride CdTe has been well demonstrated as one of the promising photovoltaic
25 material for solar cells because of its near-optimal physical properties and the ability to produce thin
26 film photovoltaic modules economically. Recently, power conversion efficiency more than 22 %
27 was reported for polycrystalline CdTe cells [1]. However despite several decades of research, this
28 efficiency is still well below the theoretical limits for CdTe, especially in terms of open-circuit
29 voltage (V_{OC}), leaving many opportunities for further optimizing materials properties and device
30 performance.

31 Today's polycrystalline devices utilize Cu, Cl and Te-rich conditions to reach 10^{14} - 10^{15} cm⁻³
32 doping by Cu substituting on Cd site (Cu_{Cd}) and the acceptor complex of Cd vacancy (V_{Cd}) + Cl
33 substituting on Te site (Cl_{Te}) (A-center) with minority electron lifetime 1-10 ns – values which have
34 held V_{OC} below 900 meV for decades [2-4]. From this state of the art, the most important variables
35 to optimize for maximizing V_{OC} are the *p*-type doping concentration and minority carrier lifetime.
36 Increasing the doping will lower the Fermi level and thus hole quasi-Fermi level allows V_{OC} to
37 increase by 60 meV/decade of doping. Increasing the minority carrier lifetime will lead to
38 increases in both short-circuit current (J_{SC}) and V_{OC} . Given the roadblocks with Cu doping and
39 Te-rich conditions [5-7], it is critical to experimentally understand and manipulate point defect
40 physics in CdTe. The *p*-type doping with groups I and V elements on (respectively) the Cd and Te
41 sites have been reported experimentally for several decades. The understanding of doping in CdTe
42 and its coupling to minority carrier lifetime via Shockly-Reed-Hall recombination has been
43 significantly advanced recently by computational efforts [5, 6]. The *p*-type doping can be obtained

44 when group-IA and-IB elements substitute for Cd under Te-rich condition or when group-V
45 elements replace Te under Cd-rich condition. Under Te-rich conditions the V_{Cd} and Te on Cd
46 antisite (Te_{Cd}) are dominant [5-7]. Cu_{Cd} will replace some V_{Cd} although the Cu can self-compensate
47 by the formation of interstitial Cu_i as well as charged native defects and both V_{Cd} and Cu_{Cd} have
48 large ionization energies >150 meV which suppresses doping efficacy (holes/ dopant atom) [5, 6].
49 Thus p -type doping is limited to less than approximately 10^{15} cm^{-3} [8, 9]. Additionally Cu diffuses
50 and drifts quickly even at solar cell operating temperatures causing device instability [10, 11].
51 Group-I elements form deep acceptors located at 100-350 meV above the valence band, which can
52 reduce lifetime [12, 13]. In addition, Te_{Cd} antisite defect can be formed easily under Te-rich
53 condition, which are likely Shockley-Read-Hall recombination centers that will limit carrier lifetime
54 [5-7]. Thus Group I doping and Te-rich conditions are not believed to offer a path forward for
55 increasing V_{OC} .

56 On the other hand, Cd-rich conditions have yielded promising results for simultaneously
57 increasing doping and lifetime. Recently, the combination of experimental and theoretical studies
58 reveals that Cd-rich condition leads long minority carrier lifetimes exceeding 20 ns [7]. This is
59 attributed to the suppression of Te_{Cd} recombination centers in Cd-rich conditions. In terms of
60 enhancement of hole concentration, recent results have indicated that phosphorous P_{Te} group-V
61 doping under Cd-rich conditions can achieve hole concentrations exceeding 10^{17} cm^{-3} [14]. CdTe
62 solar cells using P-doped bulk crystals as the absorber layer and exhibiting $V_{OC} >1$ V have been
63 reported [14], providing strong evidence for the approach. The group-V elements of N, P, As, Sb
64 and Bi substituting on Te sites create single acceptor levels with ionization energies close to 56, 68,

92, 262 and 300 from experimental [15, 16, 17] and 10, 50, 100, 230 and 300 meV from theoretical studies, respectively [5]. Although the N_{Te} acceptor has the lowest ionization energy, it is practically very difficult to incorporate into II-VI compounds except by using low temperature epitaxy. Sb and Bi are known experimentally and theoretically to have very low ionized fractions at operating temperatures because their activation energies more than 200 meV. Therefore, As and P are good candidates for p -type doping under Cd-rich conditions. Considering its lower ionization energy and predicted lower tendency for AX center behavior, as of now P seems to be the better group-V candidate. However considering from diffusion process in CdTe, it has been reported that P have a faster diffusion mechanism than As [18-20], thus P_{Te} acceptors may prove to be unstable in devices especially in the presence of grain boundaries. Therefore the properties of As-doping in Cd-rich conditions should be revealed. As-doping of CdTe has been treated in several papers. From electrical and optical properties, As-doped CdTe epilayers grown by molecular beam epitaxy indicate hole concentrations ranged from 10^{14} to 10^{18} cm^{-3} and hole mobilities of about 30-70 cm^2/Vs at room temperature by using Hall effect measurement, As_{Te} acceptor ionization energy of about 60 and 90 meV by using photoluminescence measurement [21, 22]. In addition, As_2Te_3 compound is used as intermediate layer to increase p -type doping and optimize band offset close to back contact in CdTe solar cell for improvement of Ohmic property, which makes thin p^+ layer and reduces the barrier height at back contact [23].

The traveling heater method (THM) technique has proven ability to grow large diameter CdTe with good composition uniformity and better yield [24] than Bridgman. Because of the small liquid volume compared to the feed polycrystalline charge, more uniform properties can be established

86 along the length of a grown crystal. Because the melting temperature of the saturated solvent is
87 lower than the CdTe melting point, THM offers advantages over growth techniques in which the
88 entire charge is melted at once. In case of lower growth temperature, the issues related to vapor
89 pressure during growth are excluded. There is less contamination from the crucible, the reduced risk
90 of ampoule explosion and less defect density. Te is mainly used as the solvent for the growth of
91 CdTe single crystals by THM which is used for CdTe bulk crystal for X-ray and particle detectors,
92 and many studies have been reported. On the other hand, there are few reports on the growth of
93 CdTe bulk crystals by using Cd solvent because of Cd indicates high vapor pressure which may
94 cause the explosion during growth. It could be expected the Cd-rich composition of CdTe crystals
95 by using Cd solvent THM technique. In one known publication Triboulet *et al.* have reported CdTe
96 bulk crystals using Cd as a solvent to compare the physical properties with crystals grown by a Te
97 solution, but there still are not enough deep understandings [25].

98 Considering the aforementioned experimental and theoretical results, experimental work on
99 group-V doped CdTe single crystals with Cd-rich conditions is needed to determine the limits of
100 doping and lifetime that can coexist in order to inform work on transferring such doping into thin
101 film solar cells. In this work we first investigate the influence of THM growth conditions using Cd
102 solvent on the liquid-solid interface shape and crystal quality. Then we investigate doping with As
103 by varying the As concentration. These findings will help to establish the fundamentals of group-V
104 doping in CdTe to allow eventual use of single crystal wafers as either highly-doped substrates or in
105 transferring group-V doping to polycrystalline layers for thin film photovoltaics.

106

107 **2. Experimental procedure**

108 First, feed polycrystalline ingots of CdTe were prepared by melting and reacting elemental Cd
109 (99.999%) and Te (99.999%) shots which were chemically etched to remove surface contamination.
110 Cd was etched with HCl solution for 60 seconds and then rinsed in ultrapure 18 MOhm water. Te
111 was etched in H₂SO₄ solution for 5 minutes and then rinsed in ultrapure water. The prescribed
112 amounts of elements were loaded into a carbon-coated 2 mm wall thickness quartz ampoule with 9
113 mm inner diameter under high vacuum of $\sim 10^{-6}$ Torr and then sealed off. In a vertical furnace, the
114 sealed ampoule was heated at 200 °C/h to 650 °C and held at this temperature for 24 h to react the
115 constituents and prevent explosion from the Cd overpressure. Then the sealed ampoule was heated
116 at 80°C/h to 1100 °C and held at this temperature for 24 h to complete the reaction and ensure
117 homogenization. The ampoule was then removed from the vertical furnace and allowed to cool
118 rapidly in air. The feed polycrystalline CdTe ingot, Cd solvent and As shot (99.999%) were loaded
119 into a carbon-coated quartz ampoule with 10 mm inner diameter and 2 mm wall thickness. The
120 ampoule was sealed under high vacuum (10^{-6} Torr) and then passed slowly through the hot zone of
121 the THM furnace for the crystal growth. Grown crystals were cut with a diamond blade and
122 polished mechanically with 0.01 μ m Al₂O₃ powder and then etched with a 5 % Br₂/Methanol
123 solution for 5 minutes to remove saw and polishing damage before conducting measurements.
124 The cross-sectional morphology and average composition of the samples were analyzed by optical
125 microscopy and a FEI Quanta 600F scanning electron microscopy (SEM) equipped with energy
126 dispersive X-ray spectroscopy (EDS). The As dopant and impurity concentration in the grown
127 crystals was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES;

128 SII Nano Technology SPS3520UV). Samples were dissolved into a mixed acid containing 1.2 mol
129 L^{-1} HNO_3 and 0.3 mol L^{-1} HCl . The structural properties were measured by powder X-ray
130 diffraction (XRD; Bruker D2 Phaser) after grinding the bulk crystal. The tube voltage, tube current,
131 and step width were 30 kV, 10 mA, and 0.01° and $\text{Cu-K}_{\alpha 1}$ radiation was used. The electrical
132 properties of all samples were measured using capacitance-voltage (CV; Keithley 4200-SCS)
133 measurement at room temperature. Schottky diode structures of 1 mm diameter Al Schottky
134 contact/CdTe/Ni-W Ohmic back contact were fabricated by DC sputtering through a shadow mask
135 for CV measurement. The thickness of contacts was 200–300 nm. All samples for CV were
136 annealed at 250 °C under 90% N_2 – 10% H_2 mixed gas for 10 minutes to form the contacts. CV
137 measurements used an RMS AC voltage of 30 mV and frequency of 1 MHz in the DC bias range of
138 -2 to 2 V.

139

140 **3. Results and discussion**

141 ***3.1 Growth condition for THM***

142 The stoichiometric polycrystalline CdTe solute ingots weighed approximately 15 g, and the
143 desired weight of Cd solvent was 50 mol%. From Cd-Te phase diagram [26], the liquidus
144 temperature rises steeply from the Cd endpoint upon addition of small amounts of CdTe which
145 means that growth at low temperatures is confined to dilute solutions and results in growth of small
146 crystals compared to the total volume. High temperatures still below the CdTe melting temperature
147 can be utilized to grow large crystals compared to the ampoule volume. However, the slow
148 variation of liquidus temperature with composition on the CdTe-rich side implies that small

149 temperature fluctuations will lead to significant composition variations. To balance all of these
150 competing factors we selected to use 50 mol% Cd solvent + 50 mol% CdTe solute. The temperature
151 gradient along the THM furnace axis is controlled by three coil heaters (upper, main, and bottom).
152 The upper heater is used to prevent condensation of Cd on the colder walls of the ampoule which
153 could lead to Cd deficiency. The main heater temperature (growth temperature) was 950 °C which
154 is higher than liquidus temperature. Again because of the high Cd vapor pressure, the ampoule
155 loaded with the stoichiometric CdTe polycrystalline and Cd solvent was kept at 650 °C for 24 hours
156 such that it equilibrated as liquid+CdTe phase before heating up to the growth temperature. The
157 ampoule was then lowered through the 3 zones of the furnace at 3-4 mm/day for the crystal growth.

158

159 ***3. 2 Interface between grown crystal and solution***

160 Figure 1 is an image of one CdTe ingot which was stopped in the middle of growth to reveal
161 the Cd/CdTe interface shape. A well-defined Cd solvent zone is present which can be used for
162 growth of CdTe single crystals. We focused first on the shape of the solid-liquid interface which
163 affects the quality of the grown crystals. The detailed shape of the interface, which for this slow
164 growth follows the liquidus isotherm, is governed by many parameters such as growth temperature,
165 temperature gradient, growth speed, heat flow in the charge and ampoule, and the amount of solvent.
166 In this study, we controlled the interface shape by the temperature gradient at the bottom of the
167 furnace where solidification occurs as the ampoule is lowered. New grains form and grow in a
168 direction normal to the solid-liquid interface and those heterogeneously nucleating on the ampoule
169 walls must be suppressed in order to achieve single crystals. In case of a concave liquid/solid

170 interface, new grains grow towards the center of the growing crystal resulting in polycrystalline
171 growth. On the other hand, a convex interface causes any wall-nucleated grains to grow outwards
172 preventing the polycrystalline breakdown of the crystal. A nearly flat interface is not as stable with
173 regards to polycrystalline breakdown of the growth front however it can still result in the growth of
174 large single crystals.

175 Two temperature profiles of the vertically-oriented furnace bore measured with an ampoule
176 present are shown in Fig. 2. The temperature profile A results from heater temperatures of upper
177 800 °C, main 950 °C, and bottom 750 °C. The temperature gradient between the main and bottom
178 heaters (which controls the width of the liquid zone) was about 35 °C/cm which yields a cooling
179 rate of 1.6×10^{-4} °C/s for the 4 mm/day growth rate. Figure 3 (a) (c) (e) shows a typical
180 cross-sectional view of the solid-liquid interface, a wafer cut perpendicular to the growth direction
181 and a magnified regions close to the interface by SEM grown from temperature profile A which
182 resulted in a concave interface between the Cd solution and CdTe crystal. The preparation of
183 surface in Fig. 3 is mechanically polished only before EDS measurement. Small 1-3 mm grains and
184 Cd inclusions are observed in the wafer and cross sections which demonstrates the instability of the
185 growth interface for these growth conditions.

186 It is well known that CdTe crystals grown from Te solvent contain Te precipitates or inclusions
187 [27]. Cd precipitates and inclusions have not been investigated as much as Te ones because of the
188 dominance of Te-rich melt or solution growth. However, Cd inclusions in CdTe crystals grown
189 from Cd-rich melts by the vertical Bridgman method were reported to usually appear in
190 transmission infrared microscopy imaging as six-point stars with sizes as large as 10-200 μm [28].

191 Table I shows the composition of each position in Fig. 3 (e) which is well consistent with each
192 phases. The trapping of CdTe in Cd solution can be observed close to the interface in Fig. 3 (e).
193 Therefore the irregular interface, Cd inclusions and trapping of CdTe in Cd solution close to
194 interface are detrimental for single crystal growth.

195 For improvement of crystalline quality, we increased the temperature of the upper heater to
196 change the heat flow in solution. Wang *et al.* showed that smooth wave like interface in CdZnTe
197 crystal could be obtained by applying magnetic field during growth [29, 30]. Zhang *et al.* reported
198 from simulation that the convex interface shape can be maintained by a little heating close to
199 primary heat input during melt growth [31]. The shape of interface is governed by many parameters
200 such as growth temperature, temperature gradient and convection in melt. Because the irregular
201 concave interface can be obtained from temperature profile A, the maintaining of convection is
202 good strategy to improve interface shape. Decreasing the temperature profile of the top of the
203 furnace can suppress convection in the Cd solution, thus the upper heater temperature was changed
204 from 800 °C to 900 °C to produce the second temperature profile B shown in Fig. 2. The resulting
205 temperature gradient between the main and bottom heaters was about 40 °C/cm which yields a
206 cooling rate of 1.4×10^{-4} °C/s for the 3 mm/day growth rate. A nearly flat, smooth interface was
207 obtained with the new temperature profile and the crystal quality was improved as seen in Fig. 3 (b)
208 which shows a cross section of a boule that was stopped during growth. A large single crystal more
209 than 5 mm long was obtained from the flat smooth interface which is favorable for single crystal
210 growth as seen in Fig. 3 (d). Figure 3 (f) presents an optical micrograph of the interface morphology

211 resulting from the new temperature profile B; there is no inclusion of Cd nor is there CdTe in Cd
212 solution close to the interface in this case.

213

214 ***3. 3 Characterization of CdTe single crystals grown by Cd solution***

215 The all CdTe single crystals for each characterization can be grown from temperature profile B.
216 The uniformity of the Cd/Te composition along the growth direction measured by EDS is shown in
217 Fig. 4 for a non-doped CdTe ingot. Sample wafers were cut from the growth tip at 5 mm intervals
218 except for the end (tail) region. EDS measurements were made at 3 points from the edges and center
219 of the wafers (mechanically polished and not etched) and calibrated by stoichiometric CdTe
220 reference crystal. The error bars shown are the standard deviation of these measurements and thus
221 do not reflect the systematic error of the EDS measurement itself. Within the errors of the EDS
222 measurement, the CdTe ingots appear to be spatially homogeneous and slightly Cd-rich within +0.5
223 at.%. As-dopant and impurity concentrations levels that exceed a level more than 100 ppb in
224 samples were determined by ICP-AES measurements. The As concentrations in three CdTe crystals
225 were in the range of 10^{16} , 10^{17} and 10^{19} cm⁻³. Non- and As of 10^{17} cm⁻³ doped sample results are
226 shown in Table II. The influential impurity such as Cu and Cl in CdTe solar cell were measured less
227 than 100 ppb [2-4].

228 Figure 5 shows powder XRD patterns prepared from the non-doped and 10^{19} cm⁻³ As-doped
229 CdTe single crystals in order to search for any gross secondary phase precipitation. The XRD
230 patterns contain only major peaks corresponding to diffraction lines of the zincblende CdTe
231 structure (ICDD data #03-065-1082 CdTe) calibrated by using Si powder as a reference. No peaks

232 of any other phases or impurities are detected in the XRD patterns, including for the highest-As
233 doped sample and Cd-rich condition. A shift of the lattice peaks towards higher angles is seen with
234 As doping because the As radius is smaller than that of the Te in CdTe leading to lattice strain. The
235 lattice constant was calculated by fitting the higher angle peak positions and values of $a = 6.483 \text{ \AA}$
236 for the non-doped sample and $a = 6.477 \text{ \AA}$ for the As-doped sample were obtained.

237 The doping profiles in CdTe single crystals were obtained from CV measurements as a function
238 of depletion width W and shown in Fig. 6. The acceptor concentration N_A data indicate a U-shape
239 characteristic for As-doped CdTe samples which may due to different factors such as non-Ohmic
240 contact and the presence of deep level defects [32]. Because of the absence of a perfect Ohmic
241 contact for CdTe, the effect of the back-diode can show up under forward bias which causes
242 measured capacitance to be artificially reduced [33] leading to an apparent increase in the acceptor
243 concentration under a forward bias. At high reverse bias, the apparent increase in carrier
244 concentration at the non-Ohmic back contact can be due to reasons such as the presence of deep
245 acceptor levels, a Schottky contact, or actual increased p -type doping at the back contact. An
246 apparent contribution to the acceptor concentration from a Schottky contact can occur when trap
247 levels are populated at reverse bias because of increasing of band bending but are otherwise above
248 the Fermi level and thus unoccupied under normal conditions, leading to the right branch of the
249 U-shape. The net acceptor concentration is thus best estimated from the bottom of the U-shaped CV
250 profile in the small bias region [32]. Table III summarizes the electrical parameters of CV
251 measurement. The acceptor concentration N_A increases with increasing As concentration but
252 remains within the 10^{16} - 10^{17} cm^{-3} range for the three As-doping levels investigated. Figure 7 thus

shows the activation efficiency of As doping extracted from CV measurement as a function of As concentration. The activation efficiency of As doping in the range of less than 10^{18} cm^{-3} indicates about 5-20 %. Based on prior literature [34, 35], the activation energy of As_{Te} acceptors indicates that nearly 100% will be ionized at room temperature calculated from thermal activation law, thus we infer that higher doping causes self-compensation by AX centers [35, 36] or As forming other point defects causing the doping efficacy to decrease to less than 1 % above 10^{18} cm^{-3} of As concentration. The decreasing of hole concentration with higher group-V has also been reported in other works [14, 37]. A strategy of quenching was proposed for increasing the hole concentration further and this is the topic of our future work [9, 36].

262

263 **4. Conclusions**

In this paper we report on the growth of non-doped and As-doped Cd-rich CdTe single crystals using the traveling heater method with Cd solvent rather than the more common Te-solvent used to grow high-resistivity CdTe. Stable, flat solid-liquid interfaces were obtained by optimizing the THM furnace temperature profile for our particular geometry. The composition of the non-doped CdTe single crystals were homogeneous along the growth and radial directions and the crystals were found to be slightly Cd-rich. CV measurement at room temperature showed an apparent doping limit in the 10^{16} to 10^{17} cm^{-3} range which scales weakly with increasing As concentration in the Cd-rich CdTe samples, and the activation efficiency indicates about 5-20 % less than 10^{18} cm^{-3} of As concentration.

273

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280

281 Reference

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349

350 Figures captions

351 Figure 1 Example of the resulting CdTe ingot grown from Cd solution stopped in the middle of
352 growth.

353

354 Figure 2 Temperature profile on the axis measured with growth ampoule in THM furnace.
355 Temperature profile A upper 800 °C, main 950 °C, and bottom 750 °C, Temperature profile B
356 upper 900 °C, main 950 °C, and bottom 750 °C.

357

358 Figure 3 (a) Cross-sectional view of the solid-liquid interface grown from temperature profile A. (b)
359 Cross-sectional view of the flat interface grown from temperature profile B. (c) The 1-3 mm grains
360 of CdTe wafer grown from temperature profile A. (d) The more than 5 mm of CdTe single crystal
361 wafer containing no Cd inclusions grown from temperature profile B. (e) Magnified view of the
362 highlighted portion of (a) by SEM. (f) Magnified view of flat smooth interface in (b).

363

364 Figure 4 Composition of non-doped CdTe single crystal by EDS along the growth direction.

365

366 Figure 5 Powder XRD patterns of 10^{19} cm^{-3} As-doped and non- doped CdTe single crystals.

367

368 Figure 6 Depth profiles of the net acceptor concentration in the each As-doped CdTe estimated
369 from CV measurement at 1 MHz.

370

371 Figure 7 Acceptor concentrations versus As atomic concentration. The lines indicate the activated
372 doping concentration relative to the As concentration.

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Nagaoka et al. Fig. 1

Nagaoka et al. Fig. 2

Nagaoka et al. Fig. 3

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Nagaoka et al. Fig. 5

Nagaoka et al. Fig. 6

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Nagaoka et al. Fig.7

465 Tables

466

467 Table I Composition of each phases in Fig. 3 (e) by EDS.

468

469 Table II Concentrations for As-dopant and impurities more than 100 ppb in non- and As of 10^{17}
470 cm^{-3} doped samples obtained by ICP-AES measurements. The presence of As doping could be
471 observed.

472

473 Table III Summaries of electrical parameters in each compositional CdTe extracted from CV
474 measurement.

475

476 Table I

Number in Fig. 3 (e)	Phase	Cd [at.%]	Te [at.%]
1	Cd solution	97.34	2.66
2	Grown crystal	50.45	49.55
3	Trapping of CdTe in Cd solution	50.28	49.72
4	Cd inclusions	98.13	1.87

477
478 Table II

Element [ppb]	Non-doped	As-doped
As	-	55000
C	400	520
O	430	390
Na	175	250
Mg	120	200
Al	230	180
Si	300	450

479 Table III

CV profile		
As [cm ⁻³]	N _A [cm ⁻³]	W [nm]
3.1 × 10 ¹⁵	6.2 × 10 ¹⁵	130
8.6 × 10 ¹⁷	4.6 × 10 ¹⁶	200
1.0 × 10 ¹⁹	7.9 × 10 ¹⁶	220