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Calculation of ion energy distributions of argon excimer ions generated in helicon plasma

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A program is developed to calculate the ion energy distributions (IEDs) of Ar_2^+ making use of a simplified kinetic model with a combination of Monte Carlo method. Several coefficients are used to realize good match between the calculated and measured results. Some important assumptions are confirmed: argon excimer ions have short lifetime, hence they are formed in a short range before the collecting electrode. The excimer ions that encounter collisions will be discarded because they turn to other ion species after they collide with argon atoms. From the calculated results some plasma parameters such as the cross section or neutral density in discharge could be evaluated.

Keywords: IED, helicon, plasma sheath
PACC: 5240K, 5265

1. Introduction

Low-temperature plasmas are commonly used in the microelectronics industry to etch thin films of metals, dielectrics, and semi-conducting materials. Most of these plasmas, such as inductively coupled plasmas, capacitively coupled plasmas and helicon plasmas are excited by radio frequency (rf) electric source. As a result, the potential drop from the plasma to the substrate electrode, which accelerates the ions created in the plasma towards the substrate, is modulated by the rf interfering signal. Since ion bombardment plays an important role in etching, deposition and surface modification processes, many researchers have calculated the ion energy distributions (IEDs) in several kinds of plasmas using different methods, such as: numerical integration of motion equations,[1] Monte Carlo simulations[2] and analytical model.[3,4] In most relevant papers, researchers focused on studying the IEDs of ions such as Ar^+, Cl^-, CF_3^+, and He^+. In this paper, we will focus on the calculation and measurements of IEDs of argon excimer ion (Ar_2^+) about which we have not found any result till now. The reasons for that could be as follow: Firstly, one needs to have a mass-resolved ion energy analyser to identify different ion species; secondly, the formation of excimers is a three-body process. To obtain high efficiency rate, the pressure needs to be high, possibly on the order of about 10^5 Pa or more.[5] So in low-pressure plasmas the magnitude of excimer density could be too low to measure.

2. Experimental apparatus

Our experiments were conducted in a helicon apparatus with a mass-resolved retarding field ion energy analyser, as shown in Fig.1. It consisted of three parts: source chamber, reactor chamber and analysis chamber where the energy analyser was located. The helicon source chamber and the reactor chamber shared one pump system, and the analysis chamber had another set of pump system which could keep the pressure always lower than 10^{-4}Pa even when the source chamber was in discharge. The plasma source employed a Boswell-type antenna, which was 150mm in length and 50mm in diameter. Two coils supplied an axial static magnetic field up to 0.025T. A grounded sample holder was located in the reactor chamber for plasma processing such as etching or deposition. The distance between the sample holder and the source centre was about 40cm and the reactor chamber was about 25cm in diameter. A small orifice with a diameter 0.5mm in the middle of the sample holder permitted ions to enter the ion energy analyser, which was just located behind the sample holder and along the

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source axis, as shown in Fig.1.

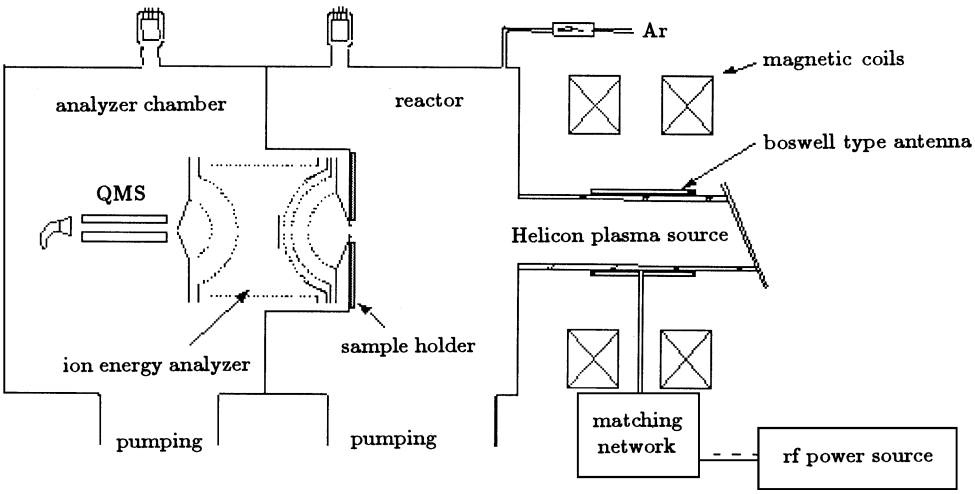


Fig.1. Diagram of experimental setup.

The energy analyser, which is just located in the analysis chamber, is a combination of a Staib-type[6] band passing spherical grid retarding field ion energy analyser and a quadruple mass spectrometer which makes the energy analyser capable of mass resolution for different kind of ions such as: Ar^+, Ar^{2+}, Ar_2^+. In this paper we will focus on the simulation and measurement of IEDs of Ar_2^+.

3. Model description

3.1. Physical and calculating model

The prototype of the kinetic model employed here comes from Ref.[7]. We will calculate the ion energy distributions of argon excimers produced in a helicon plasma apparatus making use of this model. We choose the ions generated in the range of d_s–2cm (where d_s is sheath thickness) above the collecting electrode to simulate because the sheath potential starts to saturate at 2cm away from the electrode, and Ar_2^+ will then be decomposed by a charge transfer reaction shown as follows:[8]

$$Ar + Ar_2^+ \rightarrow Ar^+ + 2Ar. \qquad (1)$$

We neglect the collisions of Ar_2^+ with other particles such as Ar^+ and e because at a distance of 40cm away from the plasma centre the neutral argon atoms are mainly particle species. To have a clear understanding of the model we use, a brief description of relevant assumptions and procedures is given below:

(a) Ions move in a constructed electric field, which will be described in detail in the next part.

(b) Excimer ions are produced in the reaction chamber (in the range of about d_s–2cm above the collecting electrode) and the ions are assumed to be produced uniformly in time and space.

(c) Ions initially have velocities determined by the Maxwellian velocity distribution function.

(d) Only one kind of collision reaction (reaction (1)) is considered in the calculation. The collision position is obtained by the Monte–Carlo method: $x_c = -\lambda \ln R$, where x_c is the length one ion will travel before the next collision happens, R is a random number, and λ is the mean free path which could be adjusted to match the calculated and measured results.

(e) Only those ions which do not encounter collision will be collected by the electrode. Ions that encounter collision will be discarded because they turn into other species after collisions.

(f) In each prescribed distance interval Δx, which is 1μm in our case, the force acting on an ion is held constant.

(g) The velocity of an ion at the end of the last interval is used to calculate the IED, and the width of the energy bin for counting ΔE is 0.1eV in the calculation.

We assume that the average electric potential in the sheath and pre-sheath is one-dimensional and vary as a function of position x, i.e., $V(x)$, and it also yields the average electric field $E(x)$. We are considering a problem related to a rf electric-field-excited plasma, so rf modulated signal has to be taken into account.

Because the wavelength of the rf modulation (~22m) is much longer than any characteristic length in the experiment, we can assume the time variation of the potential and electric field as follows:

$$V(x,T) = V(x)\left[1+\alpha\sin(\omega T+\Phi)\right] \qquad (2)$$

and

$$E(x,T) = E(x)\left[1+\alpha\sin(\omega T+\Phi)\right], \qquad (3)$$

where $\alpha V(x)$ is the amplitude of the rf modulated signal, ω is $2\pi f$ where f is the frequency, Φ is the phase of the rf signal when the ion enters the modulated sheath, ranging from 0° to 358° in 2° steps, T is the time at some instant during the flight. Note that the rf modulated signal is neglected (α=0) before the ion enters the sheath.

The force acting on an ion could be expressed as

$$F = m\frac{\mathrm{d}v}{\mathrm{d}t} = qE(x)\left[1+\alpha\sin(\omega T+\Phi)\right], \qquad (4)$$

where m and q are the mass and charge of the ion, respectively. This equation is solved in an approximate way by using a step-by-step procedure during which the force acting on the ion is held constant as the ion moves a short prescribed distance Δx. The final velocity after each step can be obtained by integrating Eq.(4):

$$v = v_0 + \frac{q}{m}E(x)\left[1+\alpha\sin(\omega T+\Phi)\right]\Delta t, \qquad (5)$$

where Δt is the time of flight corresponding to the short distance Δx, v_0 is the initial velocity of each step, $E(x)\left[1+\alpha\sin(\omega T+\Phi)\right]$ is held constant , and T is the sum of the Δt for all earlier Δx intervals.

Noting that $v = \Delta x/\Delta t$ for each Δx interval, an expression of Δx can be obtained by integrating both sides of Eq.(5):

$$\Delta x = v_0\Delta t + \frac{q}{m}E(x)\left[1+\alpha\sin(\omega T+\Phi)\right]\frac{(\Delta t)^2}{2}. \qquad (6)$$

Equation (6) is a quadratic equation, for a prescribed Δx, Δt can be solved using square root formula. The value of Δt is then used to determine the final velocity v in Eq.(5) for the corresponding interval Δx and this value of v is used as the initial velocity v_0 for next interval. The value of Δx is subtracted from the remaining distance x to obtain a new x, and contrarily, Δt is added to the earlier T to obtain a new T for the next interval. The updated T and x bring us a new product of $qE(x)\left[1+\alpha\sin(\omega T+\Phi)\right]$ which is the force acting on the ion for next interval. The process is repeated until the distance left is less than one Δx and we assume that the ion has arrived at the destination. The final velocity when the ion reaches the electrode is used to calculate the ion energy for IED.

3.2. Average potential construction

We now construct a whole plasma potential profile to replace $V(x)$ in part A by connecting two separate potential profiles for different parts: sheath region and pre-sheath region, respectively. We make use of the potential profile measurement by Miller *et al* [9] for pre-sheath region, and the simulation by Fivaz *et al* [10] for sheath region. Miller's measurement is fitted with a formula of the form as below:

$$V_{\mathrm{M}}(x) = a + b\ln(x) + c\left[\ln(x)\right]^2, \qquad (7)$$

where a, b and c are equal to 32.77, 3.743 and 0.175, respectively, in units of volt, and x is in units of meter.

The potential between the collecting electrode and where it meets Miller's measurement is modelled with Fivaz's form:

$$V_{\mathrm{F}}(x) = -(V_{\mathrm{s}}-d)\left(\frac{x-x_{\mathrm{s}}}{x_{\mathrm{s}}}\right)^2 + d\frac{x-x_{\mathrm{s}}}{x_{\mathrm{s}}} + V_{\mathrm{s}}, \qquad (8)$$

where V_{s} is the potential where $V_{\mathrm{M}}(x)$ and $V_{\mathrm{F}}(x)$ meet at the point of a distance x_{s} away from the electrode; d is used to match the gradient of $V_{\mathrm{F}}(x)$ with that of $V_{\mathrm{M}}(x)$ at the meeting point, and it varies with different value of x_{s}. As discussed later, x_{s} is used to adjust the meeting point of the two potentials, hence to vary the width of the sheath, and eventually to vary the profile of the IED. Usually x_{s} is of the magnitude of millimeter, possibly higher or lower for different parameters of plasmas and discharges. Miller *et al*'s measurements were obtained under a pressure 1.33Pa and rf power 150W, and x_{s} under this condition is around 1mm. Since our experiments were executed under a pressure 0.5Pa and power higher than 500W, and the helicon plasma was of a low pressure, high-ionization efficiency, hence a high-density plasma, we believe the value of x_{s} under our condition is smaller than 1mm. Accordingly, the magnitude of plasma potential in our experiments is also higher than that in Miller's measurements. So a scaling factor β is introduced in the calculation to adjust the peak position of the IED profile, accordingly, Eqs.(1) and (2) may be written as:

$$V'(x,T) = \beta V(x)\left[1+\alpha\sin(\omega T+\Phi)\right], \qquad (2a)$$

$$E'(x,T) = \beta E(x)\left[1 + \alpha \sin(\omega T + \Phi)\right], \qquad (3a)$$

where $E(x)$ in Eq.(3a) is the negative gradient of $V(x)$ in Eq.(2a). In calculation, the negative gradients of the potential forms by Miller *et al* and Fivaz *et al* are expressed as:

$$E_{\mathrm{M}}(x) = -\beta \frac{b + 2c\ln x}{x}, \qquad (9)$$

$$E_{\mathrm{F}}(x) = -\beta\left(-\left(-(V_{\mathrm{s}} - d)\frac{2(x - x_{\mathrm{s}})}{x_{\mathrm{s}}^2}\right) + \frac{d}{x_{\mathrm{s}}}\right). \qquad (10)$$

The minus in these two equations means that the electric field near the electrode points from plasma to electrode, and β is the scaling factor as mentioned before. To simplify for expression, we omit the sign "–" and assume β=1 for the moment. As discussed earlier, $E_{\mathrm{M}}(x)$ and $E_{\mathrm{F}}(x)$ have to match at the meeting point x_{s}, we have: $d = x_{\mathrm{s}} E_{\mathrm{M}}(x_{\mathrm{s}})$. We can see that the parameter d is uniquely determined when x_{s} is given. Equations (9) and (10) are the forces exerted on the ions as they travel through the regions $x_{\mathrm{s}} < x < 2.0$ and $0 < x \leq x_{\mathrm{s}}$ cm respectively. The whole average electric field is shown in Fig.2. Note that in this figure x_{s}=1mm, and β=1.

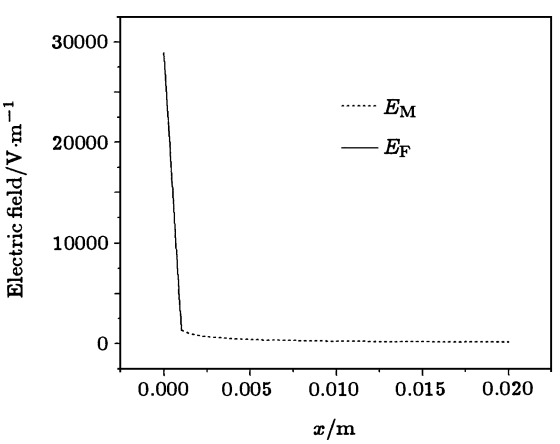


Fig.2. The average electric field composed of two parts: E_{F} ($x \leq$ 1mm) and E_{M} ($x >$ 1mm), where β=1 and x_{s}=1mm.

4. Results and discussion

Figure 3 shows a good agreement between the calculated and measured results for different discharge parameters. The solid lines are calculated results and the scatters are measured results. The measured IEDs were obtained under the same pressure and axial confined magnetic field, 0.5Pa and 0.2T. The rf powers for the discharge are 500, 1000 and 1500W, respectively. Figure 3 shows that the IED peak position moves upward as the rf power increases because higher rf power brings about higher plasma density, and thus higher average sheath potential. Higher rf power also brings about higher rf modulated signal, and therefore wider IED widths. Several coefficients are applied in the calculations to obtain good match, as shown in Table 1. To say briefly, α, a factor for varying the magnitude of modulated rf signal, is effective mainly for adjusting the width of the IED; β, a factor for varying the sheath potential, is effective for adjusting the peak position of the IED; x_{s}, the meeting point of the two electric fields, affects the sheath thickness; λ, the mean free path, together with x_{s} adjusts the profile of the IED. The different functions of these coefficients could be clearly seen in Fig.4. Combination of the adjustments of these coefficients achieves a good match between the measurements and calculations. To use the measured results obtained at rf power 1000W as an example, Fig.4 shows the deviations from good match when one of the coefficients is increased or decreased while the others keep the same values as in Table 1: (a) α changed; (b) β changed; (c) x_{s} changed; (d) λ changed.

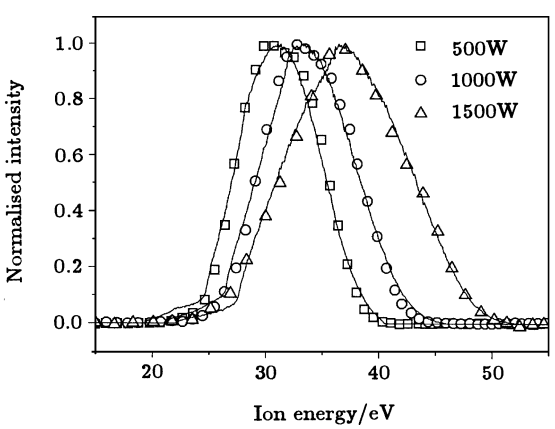


Fig.3. Good agreement between the calculated (solid lines) and measured (scatters) IEDs of Ar_2^+ for different rf powers, with pressure 0.5Pa and axial magnetic field 0.2T.

Table 1. Values of coefficients for good match between the calculated and measured IEDs of argon excimer ions for different rf power.

P_{rf}/W	α	β	x_{s}/mm	λ/cm
500	0.15	1.83	0.50	0.42
1000	0.18	2.04	0.45	0.29
1500	0.21	2.26	0.32	0.28

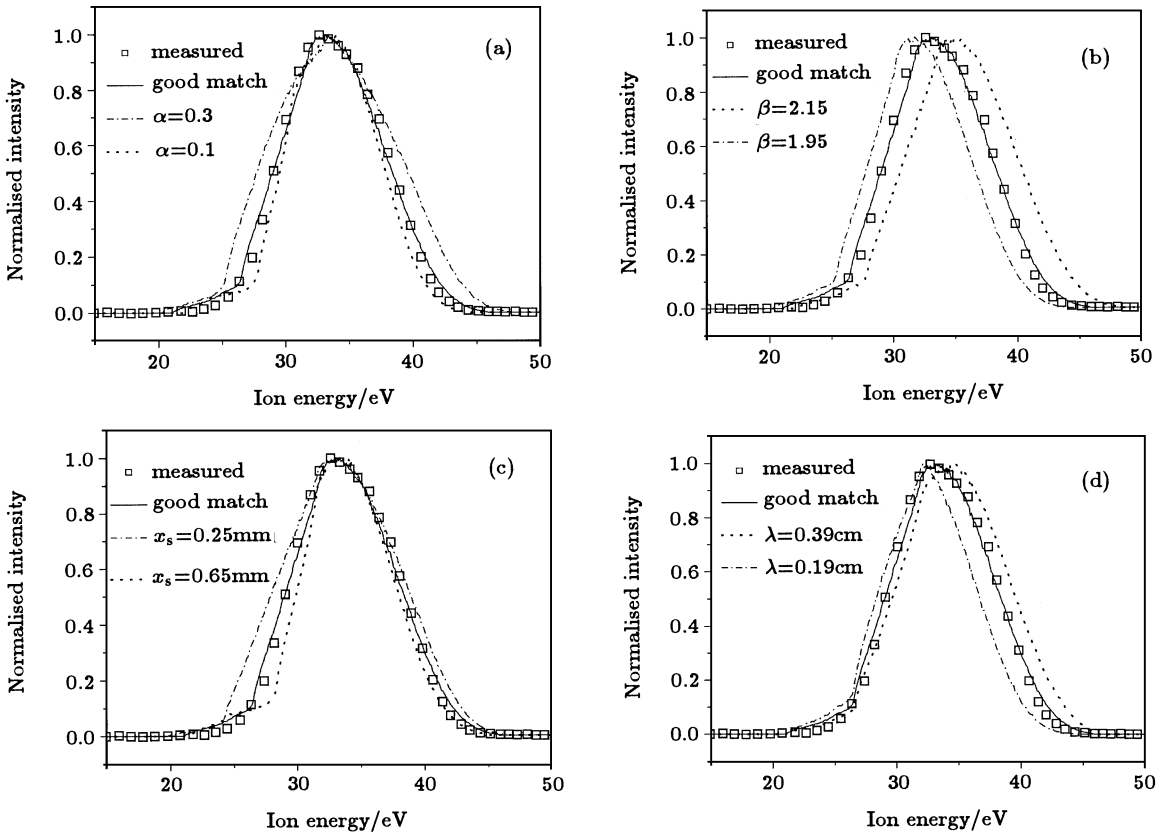


Fig.4. Deviations from good match when one of the coefficients is increased or decreased while the others keep the same values as in Table 1: (a) α changed; (b) β changed; (c) x_s changed; (d) λ changed.

In calculation we assume that only those ions which do not encounter collisions are collected by the analyser. The ions which encounter collisions turn to other particle species after the collisions. We only take into account the collisions of Ar_2^+ with argon atoms because in reactor chamber the density of neutral argon is much higher than that of plasma. In fact, we could evaluate the exact density of neutral argon in discharge from our calculated result if we know the exact cross section of reaction (1). Or, conversely, if we use the density before discharge to substitute for that in discharge, we could evaluate the cross section of a collision reaction. Note that

$$n = \frac{1}{\lambda\sigma}, \tag{11}$$

where n is the neutral density in discharge, σ is the cross section, and λ is the mean free path. But till now we have not found any experimented data on the cross section for reaction (1), fortunately we found the cross section of another similar reaction,[11] that is,

$$Kr + Ar_2^+ \rightarrow Kr^+ + 2Ar, \tag{12}$$

the cross section for this reaction is $3.75\times10^{-14}\mathrm{cm}^{-2}$.[11] However, the cross section of charge transfer reaction has a theoretical expression in the intermediate velocity range (10^5–10^8cm/s),[12] showing

$$\sigma \sim \frac{1}{\varepsilon_{iz}}\left(C_1 - C_2 \ln v\right)^2, \tag{13}$$

where ε_{iz} is the ionization energy of the neutral atom, v is the velocity of the ion and C_1 and C_2 are constants. Note that the ionization energy of Ar and Kr are 15.76 and 13.999eV, respectively. So the neutral density in the reactor chamber could be deduced to be $7.5\times10^{13}\mathrm{cm}^{-3}$ according to Eqs.(11) and (13). Compare it with the neutral density before discharge, $1.2\times10^{14}\mathrm{cm}^{-3}$ (0.5Pa), the density in discharge evaluated from our calculated results is in a reasonable error range. Conversely, if we use the density before discharge, $1.2\times10^{14}\mathrm{cm}^{-3}$ (0.5Pa), to evaluate the cross section of reaction (1), the value of σ is about $2.1\times10^{-14}\mathrm{cm}^{-2}$. Compare it with the cross section of a similar reaction mentioned above, it is also in a reasonable magnitude range.

In this paper we assume that the excimer ions are generated in a short distance range of d_s–2cm above the collecting electrode. Firstly, the excimers have short lifetime; secondly, the plasma potential starts to saturate around this distance. In fact, the plasma

potential in our apparatus is not flat after this saturation area. The potential in centre source chamber may be about tens of volts higher than that in the reactor chamber,[13] the exact potential drop depends on the experimental setup. But the argon ions do not have so high energies after they traverse the potential drop because of the collisions associated with the plasma expansion. Though the pressure in our experiment is only 0.5Pa, it is high enough to cool the accelerated ions. Fortunately, the initial average temperature does not affect the final IED profile too much since the sheath potential drop is much higher than the initial average ion energy. In calculation we assume that the Ar_2^+ ions are produced with a temperature of 600K, and the initial velocities are of Maxwellian distribution.

There could be some defects in our calculations. For example, we only take into account the excimer ions generated on the axis of the reaction chamber and neglect the ions generated elsewhere. Note that we assume the excimer ions being generated in the distance range of d_s–2 cm, so it is reasonable to think that ions produced elsewhere will depart from the axis and not be collected by the analyser, therefore we believe the approximation is acceptable and the calculated results are reliable. Another point we would like to mention is that the agreement between the calculated and measured results is decided visually. It could be more scientific if a proper method, like the least square method, is introduced to realize optimization, which we may consider in future work.

5. Conclusion

We have successfully detected the ion energy distributions of argon excimers by using a mass-resolved retarding field ion energy analyser in a helicon plasma apparatus. The IED peak position moves upward as the rf power increases because higher rf power brings about higher plasma density, and hence higher average sheath potential. Higher rf power also brings about higher rf modulated signal, and hence wider IED widths. We simulate the IEDs of argon excimers making use of a simplified kinetic model, where four coefficients, α, β, x_s and λ, are used to adjust the profiles of simulated IEDs to match that of measured IEDs. Basically, α is used to adjust the width of the IED, β is for the peak position of the IED, and x_s and λ for the profile of the IED. The simulated results fit the measured results very well for proper adjusted parameters. Though argon excimers are usually reported to exist in high-pressure plasmas, we believe that there are a few number of argon excimers in low-temperature, low-pressure argon plasmas, such as helicon plasma. But, as the calculated results approve: they have a short lifetime, so the ions collected by the electrode are produced in a short distance range near to the collecting electrode, and only those ions which do not encounter collisions could be collected by the electrode. The analysis shows that the results are reliable and the calculated results could also be used to evaluate some plasma parameters such as the cross section or neutral density in discharge.

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