Field-emission in diamond-like carbon films grown by various techniques

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The field-emission measurements from ~0.5 µm thick hydrogenated amorphous carbon (diamond-like carbon) films grown by a variety of easily implementable plasma enhanced chemical vapour deposition (PECVD) based techniques and also by a method that uses a saddle-field fast atom beam source, have been reported. Field-emission behaviour in these materials has been discussed in the light of residual stress, hardness, optical bandgap, and characteristic energy of band tails (Urbach energy). Onset emission fields as low as ~6 V/µm, together with low residual stress of 0.25 GPa, hardness of 17.5 GPa, optical bandgap of 1.5 eV and Urbach energy of 165 meV, have been obtained in diamond-like carbon films grown by pulsed-PECVD at 13.56 MHz. DLC films of comparable quality could also be grown using a saddle-field fast atom beam source, which operates on modest dc power supply and with no heated filaments or magnets.

1 Introduction

Field-emission from diamond, diamond-like, and various other forms of carbon is of considerable interest to scientists and technologists. It has been established that, DLC films containing the combined sp², sp³ hybrid bonds possess far superior electron field-emission properties than those of diamond films of purely sp² bonds. This superior emission is attributed to the abundance of sp² clusters acting as emission sites embedded in an sp³ matrix that acts as an electron conduction path using ultraviolet (UV)-Raman spectroscopy, found improved emission properties for those films that have less clearly identified diamond peaks and strongly accentuated graphitic or amorphous carbon peaks. The Motorola group, at the 1998 International Conference on Metallic Coatings and Thin Films in San Diego, reported that, 'nano-coraline' carbon is a potential candidate as a carbon cathode for field-emission displays at low electric fields, having very high emission site densities (10⁷ sites/cm² at 25 V/µm). Thus, it is clear that, diamond or high sp³-containing DLC is not an essential requirement of a cathode material for field-emission displays.

It is apparent that, for a material to be tailored for field-emission devices, one needs to consider parameters other than, threshold field and density of emission sites, such as, optical bandgap and other tribologically important film property indicators such as, hardness and stress, as well. For most such amorphous semiconductors, the value of Urbach energy, \( E_o \), appears to be an important material property indicator as seen in case of hydrogenated amorphous silicon (a-Si:H) films. However, its relevance so far, has not been examined in great detail in the a-C:H system. Thus, it may be worthwhile to closely examine the correlation of Urbach energy \( E_o \) and threshold field \( E_{th} \) for field-emission in the a-C:H system.

DLC films have been grown by a number of PECVD-based techniques and also by a method that uses a saddle-field fast atom beam source, which requires only a modest dc supply and involves no heated filaments or magnets. In the present study, the field-emission in diamond-like carbon films grown by various techniques and discuss field-emission behaviour in light of residual stress, hardness, optical bandgap and characteristic energy of band tails (Urbach energy), is reported. It is observed that, DLC films grown by these techniques not only show reasonably high field-emission at low electric fields, but also, they possess low residual stress, which may lead to high mechanical stability and reduced ageing of such cathodes when used in a device.

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2 Experimental Details

Hydrogenated amorphous carbon (a-C:H) (diamond-like carbon) films were deposited using four different techniques, at room temperature, on cleaned-polished silicon wafers and on 7059 glass substrates, using C2H2 gas as feedstock. The four techniques used were: rf (13.56 MHz) PECVD, VHF (100 MHz) PECVD, pulsed (13.56 MHz) PECVD, and a technique using a saddle-field fast atom beam source. Details of all these four techniques used for growing DLC films have already been described elsewhere. In brief, the first three techniques are basically a capacitively-coupled asymmetric PECVD technique in which, the frequency of the applied power is different, i.e., the cathode (power electrode) is connected to an rf (continuous and pulsed)/VHF power generator. The last technique essentially uses a DC plasma beam source that is mounted inside a conventional 30 cm diameter vacuum system. For VHF-PECVD, the films were also deposited using externally applied negative dc voltage, coupled with VHF power applied to the cathode, to grow sufficiently hard films. The deposition conditions used for rf continuous, rf pulse, and VHF discharge were as follows: (i) applied power density = 0.1-0.42 W/cm² (used for rf continuous and VHF discharge), (ii) ON power density = 0.42-2.0 W/cm² (used for pulsed discharge), (iii) dwell time = 150 ms, duty cycle = 30% (used for pulsed discharge), and (iv) substrate temperature = no deliberate heating. Before starting the actual process, an argon discharge was maintained at 50 W rf power for about 10 min to remove the surface impurities from the substrates by the energetic argon ions. Subsequently, the hydrocarbon gas C2H2 (Matheson Gas Products, USA) was introduced into the chamber, and the pressure was adjusted, using a Baratron (MKS type 127A) and throttle valve controller (MKS type 252 C).

A number of measurements on DLC films grown this way, were carried out. The films of ~0.5 μm thickness were deposited for this purpose. The thickness of these films was measured using a Talystep thickness profiler (Rank-Taylor and Hobson). The values of intrinsic stress in these films were evaluated from the curvature induced in the substrates due to the deposited films. The curvature was measured, using a laser scanning technique. A Knoop hardness indentor (equipped with a Zwick 3212 instrument) was used for the hardness measurement at a 50 g load. Optical transmission measurements were carried out on these films, using a Shimadzu (model 3101 PC) spectrophotometer, and the value of the optical bandgap (Eg) was evaluated from the intercept of Tauc's plot of \( \alpha(h\nu) \) versus \( h\nu \) curve (where \( \alpha \) is the absorption coefficient and \( h\nu \) is the photon energy). A transverse photothermal deflection spectroscopy (PDS) set-up was used for sub-gap absorption measurements, which allows an estimation of characteristic energy of band tails, or Urbach energy (\( E_u \)).

3 Results and Discussion

The field-emission measurements were carried out by a diode technique in a parallel-plate configuration with an anode of indium tin oxide-coated glass and a-C:H (diamond-like carbon) films deposited on polished silicon substrates as the cathode. The schematic of the field-emission measurement is shown in Fig. 1. The separation between the electrodes was defined by glass fiber spacers of thickness 40 μm, and the overlap area between the plate anode and the cathode was kept at ~0.12 cm². The current-voltage (I-V) characteristics were measured at room temperature, in a vacuum greater than 10⁻⁵ mbar maintained by a turbo-based vacuum system. The current density is calculated by taking the film area of the cathode, which is defined by the area of the hole in the spacers. The electric field is obtained by the voltage drop across the vacuum gap.

The current (I) versus electric field (E) plots of all the DLC films studied, prepared by the different techniques, are shown in Fig. 2. These characteristics were found to be repeatable and reproducible and large number of DLC films have been studied which were grown by the said processes and, generally, were found to show similar behaviour. Field-emission involves a quantum mechanical process in which electrons tunnel out of electrodes into vacuum, when subjected to a very high electric field. It is a non-linear process in which the emission I-V (electric field) characteristics are usually described by the classic Fowler-Nordheim (F-N) equation:

\[
I = A (\beta E)^2 \exp (-B\psi^{3/2}/\beta E)
\]
Table 1 — Properties of DLC films grown using various techniques

<table>
<thead>
<tr>
<th>Properties</th>
<th>Self-bias voltage (V)</th>
<th>Threshold field (V/μm)</th>
<th>Barrier height for emission (eV)</th>
<th>Residual stress (GPa)</th>
<th>Hardness (GPa)</th>
<th>$E_g$ (eV)</th>
<th>$E_o$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technique</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>rf-PECVD</td>
<td>-120</td>
<td>10.0</td>
<td>0.09</td>
<td>4.3</td>
<td>8.4</td>
<td>1.74</td>
<td>310</td>
</tr>
<tr>
<td>VHF-PECVD</td>
<td>-10</td>
<td>7.5</td>
<td>0.07</td>
<td>1.7</td>
<td>4.0</td>
<td>1.6</td>
<td>240</td>
</tr>
<tr>
<td>VHF-PECVD + bias</td>
<td>-(10+390)</td>
<td>8.8</td>
<td>0.10</td>
<td>2.9</td>
<td>9.0</td>
<td>1.6</td>
<td>265</td>
</tr>
<tr>
<td>pulsed-PECVD</td>
<td>-</td>
<td>6.2</td>
<td>0.06</td>
<td>0.25</td>
<td>17.5</td>
<td>1.5</td>
<td>165</td>
</tr>
<tr>
<td>saddle-field FAB</td>
<td>-</td>
<td>6.2</td>
<td>0.13</td>
<td>0.1-0.25</td>
<td>15-20</td>
<td>1.0</td>
<td>260</td>
</tr>
</tbody>
</table>

where $I$ is the current in amperes, $\phi$ is the barrier height in eV, $E$ the electric field in V/m, $\beta$ is the field enhancement factor at sharp geometries, and $B = 3.06 \times 10^6$ for carbon and $A = 1.4 \times 10^5$. The plots of $I/E^2$ versus $I/E$ for the data points shown in Fig. 2, are given in Fig. 3. The slopes of these plots give the effective emission barriers ($\phi$), if we assume an ideal plane emitter with a field enhancement factor $\beta$ of 1. The electric field corresponding to the point of inversion in the $F-N$ plots (Fig. 3) is defined as the $E_{\text{um-ON}}$ (threshold field) for field-emission from DLC films. The values of $E_{\text{um-ON}}$ (threshold field) and barrier height of emission ($\phi$), evaluated from the $F-N$ plots of all the DLC films grown by different techniques, are summarized in Table 1. The values of stress, hardness, $E_g$, and $E_o$ of all the DLC films grown by different techniques are also given in the table. The values of $E_{\text{um-ON}}$ and $\phi$ for low-stress DLC films grown by conventional rf-PECVD techniques are found to be 10.0 V/μm and 0.09 eV, respectively. Corresponding values of stress, hardness, $E_g$, and $E_o$ are 4.3 GPa, 8.4 GPa, 1.74 eV, and 310 meV, respectively. For an emission current density of $10^{-4}$ mA/cm², the $E_{\text{um-ON}}$ values for these samples are found to be 10-12 V/μm, which is similar to the values of $E_{\text{um-ON}}$ of un-doped DLC films grown by rf-PECVD technique reported in the literature.

The DLC films prepared by VHF-PECVD technique show $E_{\text{um-ON}} = 7.5$ V/μm and $\phi = 0.07$ eV. The $E_{\text{um-ON}}$, $\phi$, and $E_g$ values of DLC films grown by VHF-PECVD technique are found to be lower than the values of $E_{\text{um-ON}}$ of DLC films grown by the rf-PECVD technique. VHF-PECVD-grown DLC films are found to have lower values of stress = 1.78 GPa, hardness = 4.0 GPa, $E_g = 1.6$ eV, and $E_o = 240$ meV, as compared to the rf-PECVD-grown DLC films. These films are, thus, found to be soft in comparison to the rf-PECVD-grown films. When an additional negative bias of $= -390$ V is applied, the values of $E_{\text{um-ON}}$, $\phi$, stress, hardness, and $E_o$ are all found to increase to 8.8 V/μm, 0.10 eV, 2.9 GPa, 9.0 GPa, and 265 meV, respectively, whereas the value of $E_g$ remains at 1.6 eV. VHF-PECVD-grown DLC films with the application of additional negative bias are found to have reduced values of $E_{\text{um-ON}}$, stress, $E_g$, and $E_o$ as compared to the values obtained in rf-PECVD-grown DLC films, whereas the values of $\phi$ and hardness of VHF-PECVD-grown DLC films, on application of additional negative voltage are...
marginaly greater than those of rf-PECVD-grown DLC films \( (E_{\text{turn-ON}} = 8.8 \text{ V/}\mu\text{m} \text{ and } \phi = 0.10 \text{ eV}) \). For an emission current density of \( 10^4 \text{ mA/cm}^2 \), the \( E_{\text{turn-ON}} \) for VHF-PECVD-grown DLC films is found to be 7.5 V/\mu m; with the application of additional negative voltage, this \( E_{\text{turn-ON}} \) for the same emission current density becomes 8.8 V/\mu m, which is found to still be less than the \( E_{\text{turn-ON}} \) for conventional rf-PECVD-grown DLC films.

The DLC films grown by the pulse-PECVD technique exhibit significantly reduced \( E_{\text{turn-ON}} \) (6.2 V/\mu m), \( \phi = 0.06 \text{ eV} \), stress (0.25 GPa), \( E_p \) (1.5 eV), and \( E_o \) (165 meV) and considerable enhancement in the values of hardness (17.5 GPa), as compared to the values of these parameters obtained for DLC films grown by the conventional rf-PECVD technique. For an emission current density of \( 10^4 \text{ mA/cm}^2 \), the \( E_{\text{turn-ON}} \) for pulse-PECVD-grown DLC films is found to be 6.2 V/\mu m, which is less than the \( E_{\text{turn-ON}} \) of conventional rf-PECVD and VHF-PECVD-grown DLC films.

The DLC films grown by the saddle-field fast atom beam source technique recorded \( E_{\text{turn-ON}} = 6.2 \text{ V/}\mu\text{m} \), \( \phi = 0.13 \text{ eV} \), stress = 0.10-0.25 GPa, \( E_p \) = 1.0 eV, hardness = 15.0-20.0 GPa and \( E_o \) = 260 meV. However, saddle-field-grown DLC films have similar values of \( E_{\text{turn-ON}} \), and also, of stress and hardness; but in our preliminary experiments, these films recorded significantly higher values of \( \phi \) and \( E_p \) and a reduced value of \( E_o \), as compared to the DLC films grown by the pulse-PECVD technique. However, saddle-field-grown DLC films are found to have lower values of \( E_{\text{turn-ON}} \), stress, \( E_p \), \( E_o \) and higher values of \( \phi \), as compared to the values obtained for DLC films grown by the conventional rf-PECVD technique. For an emission current density of \( 10^4 \text{ mA/cm}^2 \).
mA/cm², the $E_{\text{rms-ON}}$ for saddle-field fast atom beam source-grown DLC films is found to be 6.2 V/µm, which is comparable to the $E_{\text{rms-ON}}$ for pulse-PECVD-grown DLC films, and this value is much lower than the $E_{\text{rms-ON}}$ of conventional rf-PECVD and VHF-PECVD-grown DLC films.

Satyanarayan et al.⁵⁸ have studied field-emission from tetrahedral amorphous carbon (ta-C) films grown by the filtered cathodic vacuum arc (FCVA) technique, and they reported that, the values of $E_{\text{rms-ON}}$ decrease with the increase of sp³ content, as well as with low levels of nitrogen content. They reported the minimum values of $E_{\text{rms-ON}}=10-12$ V/µm for an ion energy around 80-100 eV in ta-C films, and optimally nitrogen-doped (~0.4% N) films recorded $E_{\text{rms-ON}}$ values, as low as 3.5 V/µm. The effective emission barriers (φ) of 0.037-0.10 eV have been reported for ta-C films and the barrier reduces to 0.011 eV for the optimum ta-C:N film ⁵⁹. Amaratunga & Silva⁵⁵ have also studied nitrogen-containing a-C:H films grown by rf-PECVD technique with magnetic confinement, and they reported that, the onset emission field decreases with the increase of nitrogen content, and an onset emission field, as low as 4 V/µm, has been obtained in a-C:H films having 15% nitrogen content. The emission barriers (φ) of 0.03-0.05 eV have been reported by them, assuming an ideal flat-plate emitter from the F-N plots. Nitrogen incorporation in DLC films leads to the following: (i) reduction of residual stress⁶⁰-⁶⁴, (ii) reduction of optical bandgap⁶⁵, and (iii) enhancement of conductivity⁶⁶. All these factors need to be carefully understood while discussing field-emission for nitrogenated DLC films. However, the universality of stress reduction on nitrogen incorporation in the a-C:H network is well-documented⁶⁵-⁶⁷. The mechanism put forward to explain this behaviour involves replacement of a four-fold-coordinated carbon by nitrogen atoms. As the nitrogen atoms admit a coordination number equal to three at most (sp³ hybridized nitrogen), the replacement of carbon atoms by nitrogen atoms in a-C:H films necessarily implies reduction of the average coordination number. This, in turn, leads to the reduction of the degree of over-constraint, and hence, reduction of internal residual stress in the films⁶⁸. Whether or not there exists any correlation in the values of residual stress of nitrogenated DLC films and their corresponding lower $E_{\text{rms-ON}}$ values, needs to be further investigated.

The values of $E_{\text{rms-ON}}$ (~6 V/µm), obtained for the DLC films grown by the pulse-PECVD and saddle-field fast atom beam source techniques, reported in this paper, are thus found to be of comparable quality. It will be interesting to see how by nitrogenation, their field-emission behaviour can be further optimized. The values of effective emission barriers (φ) for DLC films grown by the different techniques have been found to be in the range 0.06-0.13 eV. Similar values have also been reported by others⁵⁷-⁶⁰. These values are obviously quite low, and the true barrier may be much larger. So, further work is needed to understand the slope of F-N curves. The authors have also observed, during the present investigation that, the value of $E_{\text{rms-ON}}$ decreases with the decrease of $E_g$. This is consistent with the report of Burden et al.⁵⁹ who have studied the enhancement of field-emission properties of a-C:H films by thermal annealing. Robertson & Rutter⁶⁵ state that, the increase of $E_g$ means that, conduction band of amorphous carbon approaches the vacuum level, whereas the valence band remains approximately the same. Therefore, if a space-charge-controlled mechanism is responsible for emission, to a first-order approximation, the threshold field should be proportional to the optical bandgap of a-C:H.

Now, let us look at overall performance of any field-emission device. This depends on the following: (i) the nature of the substrate material, (ii) the film, and (iii) the surface of the film. This implies that, the silicon substrates used for these studies help maintain a supply of electrons into the DLC layer, and these electrons are then transported through the DLC layer; finally, the electrons tunnel from the surface of the DLC layer into the vacuum, completing the field-emission. For better performance, steps (ii) and (iii) mentioned above require the deposition parameters of the DLC films to be chosen in such a way so that field-emission from the DLC layer can be maximized at low turn-ON fields. A satisfactory field-emission behaviour of the DLC films can probably be attributed to the presence of both graphitic and diamond carbon components, and their relative concentration determine the $E_{\text{rms}}$ and probably the electron affinity, respectively, of these films. There may be an optimum component of diamond and graphitic...
carbon in the DLC films where, these films may perform as better field emitters. Iii et al.\textsuperscript{26} while reporting the sp\textsuperscript{2} phase nano-structure on field-emission from amorphous carbons recently, stated that, the optimum size of sp\textsuperscript{2} phase is of the order of 1 nm. These authors further reported that, the size of sp\textsuperscript{2} phase can dominate the effect of chemical bonding, sp\textsuperscript{3} content or conductivity on field-emission. The authors have also observed, during the present investigations that, the values of $E_{\text{on,ON}}$ is found to decrease with the decreasing values of $E_{\text{in}}$ as well. Decrease of $E_{\text{in}}$ correlates to the increase of graphic components in the films, which promote electric conduction; lowering of $E_{\text{in}}$ presumably, leads to the decrease of the amount of disorder, which smooths the hopping transport of electrons through the DLC layer in the field-emission devices. Thus, the decrease of both $E_{\text{in}}$ and $E_{\text{on}}$ in these DLC films may lead to the enhancement of the field-emission behaviour in such devices. Again, in the defect sub-bandgap model of field-emission advanced by Huang et al.\textsuperscript{35} it is proposed that the electrons participating in the field-emission phenomenon originate from the defect sites band, located below the conduction-band minimum. Indeed, emissivity of diamond in many experiments has been found to increase with the increase of defect concentration. Gupta et al.\textsuperscript{37} while studying the electron field-emission and microstructure correlation in nano-crystalline carbon thin films stated that, along with grain-size dependence, the defects, specially, localised states within the bandgap, play a crucial role and assist in lowering the emission threshold. In view of what has been stated above, the measurement of the sub-bandgap absorption parameter, Urbach energy ($E_{\sigma}$), assumes great importance. In amorphous silicon and related alloy systems, which are mostly four-fold coordinated, the utility of this parameter has been well established. It is reported in this paper, the existence of such a correlation, at least for the films deposited by the PECVD methods (Table 1). It is emphasized here that, a rather, detailed study, based on closed parametric variation, for films grown by one particular technique, as well as nitrogen-doping studies, would be most rewarding in firmly establishing such a correlation.

Comparing the experimental data with the previous works, the authors found that, the values of $E_{\text{on,ON}}$ of DLC films, grown by various techniques mentioned in this paper, are lower than the values obtained by Park et al.\textsuperscript{3} Chuan et al.\textsuperscript{11}, and significantly lower than those of un-doped a-C:H film\textsuperscript{11}. These values are again lower than 20-60 V/\textmu m for the crater-free emission from ta-C deposited by laser ablation\textsuperscript{12} and comparable to those reported by Amarutunga & Silva\textsuperscript{13} and Satyanarayan et al.\textsuperscript{16} on nitrogen-containing a-C:H and nitrogen-doped ta-C films, respectively. For a complete field-emission device, many other consideration involving emission current available, needs to be taken into account.

Finally, our results as summarized in Table 1, seen in the context of nitrogenated a-C:H films of Amarutunga & Silva\textsuperscript{13} and nitrogenated ta-C films of Satyanarayan et al.\textsuperscript{16}, reveal the following:

(i) There appears to be a direct correlation between the reduction of residual (compressive) stress in DLC films and the lowering of the threshold field for field-emission.

(ii) Nitrogenation of a-C:H films reported by Amarutunga & Silva\textsuperscript{13} and nitrogenation of ta-C films by Satyanarayan et al.\textsuperscript{16} may, perhaps, also would have led to the reduction of built-up stress, though, this has not been explicitly mentioned by them. The results of the authors of DLC films grown differently and other results\textsuperscript{28-31} point toward this general trend. It may be noted that, on nitrogenation, Amarutunga & Silva\textsuperscript{13} and Satyanarayan et al.\textsuperscript{16} find very significant decrease in the threshold field.

(iii) Urbach energy ($E_{\sigma}$) is a measure of the extent to which a network is relaxed due to the various processing-related and post-deposition treatment. In fact, any detailed analysis of residual stress behaviour of a-C:H must necessarily identify the specific role played by structure-related disorder. The initial results of the authors, on PECVD-produced DLC films, at least, indicate the existence of a possible correlation between the reduction of $E_{\sigma}$ and the lowering of the threshold field, as revealed by the field-emission measurements.

The correlations being reported by them need further to be established on more fundamental level i.e., involving sp\textsuperscript{3}/sp\textsuperscript{2} ratio, bound and unbound hydrogen, clustering of sp\textsuperscript{2} complex etc. Since, when the process parameters are varied or deposition techniques in subtler level, these are the macroscopic parameters that change, and network
under same situation relaxes to low stress values. However, to observe these finer details of the
network, very sophisticated techniques and careful
analysis of data is required. Even for most
commonly quoted sp²/sp³ ratio, experience of the
authors and expert views show that, only high
resolution ¹³C NMR spectroscopy appears to be the
most reliable method for determining the relative
concentrations of sp² and sp³ hybridized carbon, as
well as the local environment of carbon, in each
state, in hydrogenated DLC. Electron Energy Loss
Spectroscopy (EELS) is another technique used in
determining the sp³ fraction in non-hydrogenated
DLC, especially, in so-called tetrahedral amorphous
carbon (ta-C). But this technique is, however, not
suitable for hydrogenated DLC films due to their
sensitivity towards irradiation with an electron
beam. Efforts of the authors in future will be to see
that, the given correlation that are reporting here, are
further investigated by more careful analysis.

4 Conclusion

Field-emission in diamond-like carbon films
grown by a variety of PECVD based techniques and
also by a method that uses a saddle-field fast atom
beam source have been studied. Onset emission-
field values as low as $E_{\text{onset}} \approx 6$ V/μm, together
with the low values of stress of 0.1-0.25 GPa, high
hardness of 15-20 GPa, $E_p$ of 1.0-1.5 eV, and $E_x$ in
the range of 165-260 meV, have been obtained in
DLC films grown using pulse-PECVD and saddle-
field fast atom beam source techniques. It is worth
mentioning that, the stability of the material is very
important for reproducible device applications and
significant field-emission was observed at low
threshold fields, in those DLC films which recorded
low residual stress values, as well. The authors have
found a correlation of threshold field required for
emission on residual stress, $E_p$, and $E_x$ as well, and
the values of $E_{\text{onset}}$ are found to decrease with
the decrease of residual stress, $E_x$, and $E_p$ values.

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