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Isotope composition dependence of the band-gap energy in diamond

H. Watanabe,[1,*] T. Koretsune,[2] S. Nakashima,[3] S. Saito,[2,4] and S. Shikata[5]
[1]*Correlated Electronics Group, Electronics and Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 4, 1-1-1, Higashi, Tsukuba, Ibaraki 305-8562, Japan*
[2]*Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo, 152-8551, Japan*
[3]*Advanced Power Electronics Research Center, AIST, Tsukuba Central 2-13, 1-1-1, Umezono, Tsukuba, Ibaraki 305-8568, Japan*
[4]*Materials Research Center for Element Strategy, and Research Center for Nanometer-Scale Quantum Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo, 152-8551, Japan*
[5]*Diamond Research Group, Research Institute for Ubiquitous Energy Devices, AIST, 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan*

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We present experimental results on the band-gap energies of homoepitaxial diamond films with isotopic compositions ranging from nearly pure carbon-12 (^{12}C) to nearly pure carbon-13 (^{13}C). Diamond crystals were grown by microwave plasma-assisted chemical vapor deposition, which controls the isotope composition and minimizes the density of impurities and defects. We find that the isotope substitution of ^{12}C by ^{13}C increases the band-gap energy in diamond by up to 15.4 meV at 79 K. The increase at room temperature is estimated from the temperature dependence of the band-gap renormalization due to electron-phonon interaction and is found to be even larger than that at low temperatures. These results unambiguously demonstrate the possibility of band-gap engineering of diamond via control of the isotopic composition.

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Control of compositional impurities of stable isotopes with different masses is a common requirement inherent in almost all semiconductor materials. Diamond consisting of a natural abundance of carbon isotopes [98.9% carbon-12 (^{12}C) and 1.1% carbon-13 (^{13}C)] is an indirect-gap semiconductor with a wide band gap of 5.48 eV under ambient conditions (300 K, 1 atm).[1] Variation of the isotopic composition should greatly affect the properties of phonons, especially in the case of diamond due to the light atomic mass of the carbon atom.[2–6] For example, it is well known that the thermal conductivity for a 99.9% ^{12}C diamond is 50% higher at room temperature than that of natural ^{12}C-^{13}C mixtures.[7] Control of isotope composition is, however, mostly an undeveloped area in semiconductor device applications, even for silicon.

In 2009, diamond superlattice structures composed of isotopically pure ^{12}C and ^{13}C layers were synthesized and confirmed to exhibit carrier confinement due to the isotope effect on the band-gap states of diamond.[8] These isotope-based superlattice structures offer entirely new directions in diamond research, including use for realizing a high-mobility two-dimensional carrier gas, for exciton confinement, for folding of phonon dispersion branches, and for spatially controlling nuclear spins, which should be of great importance in quantum computing applications. For the applications of an isotope diamond superlattice through electronic band-gap engineering, an important factor to be clarified is the total amount of change in band-gap energy due to isotope effects.

There have been several experimental and theoretical studies indicating large isotope effects and/or band-gap renormalization of diamond.[9–14] Pioneering research focusing on isotope composition-controlled diamond was performed by Collins *et al.* in 1990 (Ref. 12) for diamond grown using high-pressure and high-temperature (HPHT) methods. They reported that the band gap of ^{13}C-enriched diamond is greater than that of ^{12}C diamond by 13.6 meV, which is 1 to 2 orders of magnitude larger than the measured or calculated values of a number of semiconductor materials.[13–16] Later, Ruf *et al.* reported a *linear* isotope dependence of 14.6 meV/amu with varying ^{13}C content.[17] In these experiments studying isotope effects on band-gap energy, the diamond samples were synthesized via HPHT methods from various carbon-based raw materials, including solvents and catalysts, which limit the purity of the crystal. In fact, in previous cathodoluminescence (CL) studies, boron-bound exciton peaks were observed.[12,17] Furthermore, Yamaguchi *et al.* studied natural composition and ^{13}C-enriched chemical vapor-deposited (CVD) diamond particles on polycrystalline copper (Cu) substrates for the first time using CL spectroscopy and found a band-gap change of 11 meV,[18] which is smaller than the results reported earlier for HPHT diamond. Furthermore, recently, Barjion *et al.* reported that a band-gap shift of 12.2 meV was obtained using isotopic diamond homoepitaxially grown by microwave plasma CVD.[19] One reason for this discrepancy might be a difference in the relative concentration of impurity atoms and defects since the actual isotope composition dependence of band-gap energy may change quite sensitively with the quality of the diamond crystals.

In this paper is reported a CL study of ultraclean diamond samples synthesized via microwave plasma-assisted CVD in order to clarify the dependence of band-gap energy on isotope composition, $^{12}\mathrm{C}_{1-x}{}^{13}\mathrm{C}_x$ ($0 \leqslant x \leqslant 1$). Isotopically controlled homoepitaxial diamond thin films grown from isotopically enriched methane (^{12}CH$_4$ or ^{13}CH$_4$) and hydrogen (H$_2$) are used, and the microwave plasma-assisted CVD reactions have been optimized to generate samples with defect- and impurity-minimized bulk properties.[20] The Raman and CL experimental results for the mixed-isotope crystals of diamond show that the nominal C isotope ratio in the methane reagent gas agrees well with the ratio in the diamond films obtained and that tuning of the diamond band gap can be achieved with very high accuracy using the present synthetic method. The electronic band-gap shift of the isotopically enriched diamond is up to 15.4 meV, larger than all experimental values previously reported and in good agreement with the 16.5 ± 2.5 meV estimated from the temperature dependence of the band gap.[12]

Diamond films were prepared from the isotopically enriched CH_4 and H_2 mixed gas system in a microwave plasma-assisted CVD reactor. The gases have purities greater than 99.9% for ^{12}C and greater than 98.7% for ^{13}C. The substrates were HPHT synthetic type IIa (001) single-crystal diamond plates with a misorientation angle of less than 0.7° as detected by x-ray diffraction. The feed gases for this deposition system were delivered via a mass-flow controller and were premixed in the manifold before being injected into the growth chamber. The gas composition was determined from the flow rate of each gas. The growth parameters were the same as those described in our previous work.[21] The thickness of the films grown was about 4 μm.

Prior to growth, each substrate was prepolished using the scaife process[22] and cleaned by boiling in a sulfuric acid-(H_2SO_4-) based solution, ultrasonication in deionized water and alcohol-based solutions, etched in a hydrofluoric acid (HF) solution, treated with RCA SC-1 (NH_4OH:H_2O_2:H_2O = 1:1:5),[23] and finally, rinsed with deionized water. The substrate was also treated with H_2 plasma in the processing chamber for 30 min. using high-purity H_2 gas (>9 N).

The phonon frequency change of the isotopically controlled diamond films was measured via confocal micro-Raman spectroscopy based on a Jobin-Yvon model U1000 double monochromator with 1800 grooves/mm gratings, using an Ar laser working at 514.5 nm with backscattering geometry and detection with a liquid N_2-cooled charge-coupled device (CCD). The measurements were performed at room temperature. Correction of the zero drift of the spectrometer and calibration of the wave-number scale were performed using a Ne lamp standard and high-quality HPHT synthetic type IIa single-crystal diamond before and after recording the Raman spectra. The spectral resolution was better than 0.8 cm^{-1}.

The CL measurements were performed at a 9-kV acceleration voltage and a 100-nA electron beam current. The electron beam current was monitored using a Faraday cup detector assembled in the sample holder. The CL were collected by a specially designed and optimized mirror system, where the light is focused on an optical fiber bundle guiding the light into a 0.55-m monochromator (Jobin-Ybon, Model TRIAX550) with 1200 grooves/mm, blazed at 250 nm. A uv-enhanced-CCD was used as the detector. The spectral resolution was 0.04 nm (0.89 meV). The measurements were performed at a sample holder temperature of 79 K.

Figure 1 shows near-band-edge CL spectra at 79 K of diamond films grown with several selected isotope compositions in the gas phase, $^{12}C_{1-x}{}^{13}C_xH_4$, with $x = 0.001, 0.247, 0.494, 0.740$, and 0.987. The observed CL spectra, consisting of a single prominent peak, reveal an intrinsic diamond feature. There are no other peaks associated with impurities or defects. The peak originates in the annihilation of a free exciton (FE^{TO}) mediated by the transverse optical (TO) phonon having a wave vector of (0.76,0,0) $2\pi/a$, corresponding to the minima of the conduction band along the Δ-line, where a is the lattice constant. The spectra are normalized to the intensity of the FE^{TO} emission peak. The FE^{TO} emission peak, associated with the indirect band gap, shifts toward higher energy as the concentration of ^{13}C in the gas phase increases. By changing the isotope composition from nearly pure ^{12}C ($x = 0.001$) to nearly pure ^{13}C ($x = 0.987$), the peak position increases by 20.3 meV from 5.2763 to 5.2966 eV. The trend observed in Fig. 1 is in accord with the systematic experiments of Ruf *et al.*[17] on the isotopically modified HPHT diamond samples. However, the experimentally measured shift value of 20.3 meV is much larger than not only the result by Ruf *et al.* but also the excitonic band-gap shift value that we observed earlier (19 meV).[24] In the present experiment, we have removed the carbon parts as much as possible in the chamber to suppress residual carbon that might be present after the CVD process. This treatment should have suppressed the so-called "memory effect" of carbon. Consequently, the isotope purity in the CVD environment has been improved, and the largest shift of the CL peak upon the change of the isotopic composition must have been observed.

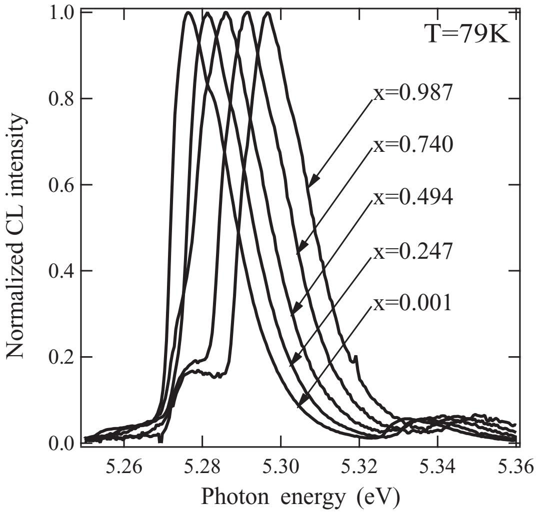

FIG. 1. Luminescence spectra of free excitons in homoepitaxial diamond films grown from mixture of methane in hydrogen by means of a microwave plasma-assisted CVD. The spectra illustrate the effects of isotope composition $^{12}C_{1-x}{}^{13}C_x$ ($x = 0.001$, 0.247, 0.494, 0.740, and 0.987) mixed in the CVD gas phase. All spectra are normalized to the same height.

Figure 2 shows superimposed Raman spectra taken at room temperature of the samples shown in Fig. 1. Each spectrum is fitted to a Lorentzian curve, and the intensities of the peaks are normalized to unity at the maximum. For nearly pure ^{12}C ($x = 0.001$), a first-order Raman frequency peak is observed at 1332.8 cm^{-1}, which is 0.3 cm^{-1} larger than the literature value of natural abundance diamond.[25] The peak position shifts to lower frequency as the ^{13}C concentration increases. As the concentration changes from nearly pure ^{12}C ($x = 0.001$) to nearly pure ^{13}C ($x = 0.987$), the frequency of the first-order Raman peak decreases by 50.8 cm^{-1}, from 1332.8 to 1282.0 cm^{-1}.

The inset of Fig. 2 depicts the frequency (ω) of the first-order Raman peak as a function of the average C isotopic mass ($\overline{M} = 12 + x$) in the isotopically mixed gas. In the classical harmonic oscillator model, the frequency of the vibrational modes of the lattice is proportional to $\overline{M}^{-1/2}$. As a matter of fact, the data for isotopically pure samples ($x = 0.001$ and

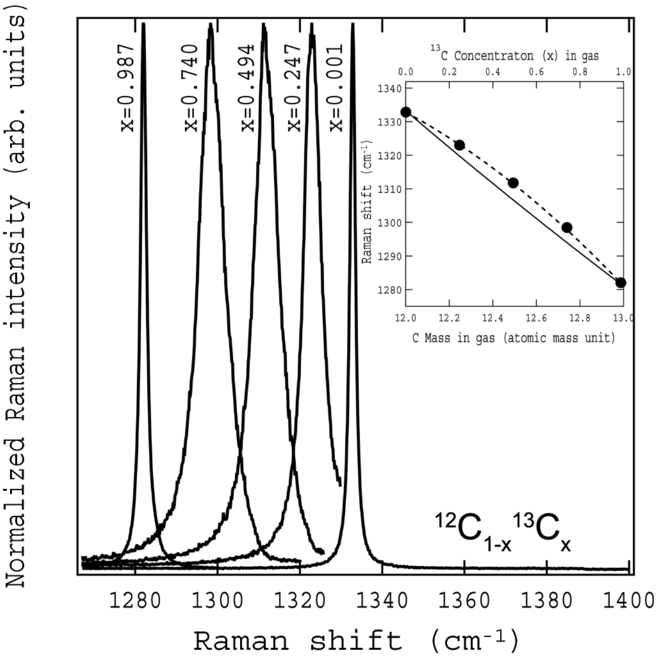

FIG. 2. First-order Raman spectra obtained from the samples used in the CL measurement (Fig. 1). The inset displays the first-order Raman peak shift as a function of ^{13}C concentration (x) in gas. The solid line represents a prediction of the harmonic approximations. The dashed line corresponds to the polynomial of Eq. (2).

0.987) fit well with one fitting parameter, C:

$$\omega = C\sqrt{12/\overline{M}}\text{cm}^{-1}, \tag{1}$$

as is shown by the solid curve in the Fig. 2 inset. Here, the fitting parameter C determined from the two extreme points is 1333.3 cm^{-1}. On the other hand, the experimental Raman shifts of samples with mixed C isotopes are slightly larger than the values expected from Eq. (1). These deviations should be due, at least partially, to isotope disorder, as will be discussed later. The peak positions of the first-order Raman spectra, including the mixed C isotope cases, are well represented by a polynomial, which is known to hold with very high accuracy experimentally[26]

$$\omega_0 = 1332.82 - 34.77x_f - 16.98x_f^2\ \text{cm}^{-1}, \tag{2}$$

where ω_0 is the position of the first-order Raman peak and x_f is the ^{13}C content of the film. It is found that the nominal isotope composition of the methane gas is in good agreement with the ^{13}C content of the film given by Eq. (2), with an accuracy of approximately 1%. Therefore, x can be considered to be essentially the same as x_f in our sample. This indicates that artificial isotope replacement in diamond can be achieved with high efficiency and high accuracy under these growth conditions. In the following discussion, Eq. (2) is used to estimate the x_f values.

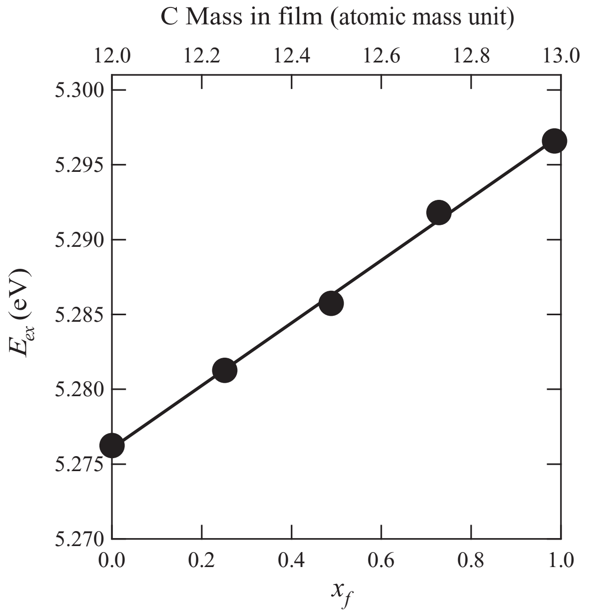

FIG. 3. Excitonic band-gap energy E_{ex} obtained for the CL peak energies in Fig. 1 as a function of the ^{13}C concentration of the films (x_f). The actual ^{13}C content of the films was calculated from the peak position of the first-order Raman spectrum. The solid line is a linear regression fit of the data.

In Fig. 3, the excitonic band-gap energy, E_{ex}, obtained as the CL peak energies in Fig. 1, is plotted as a function of the ^{13}C concentration of the films (x_f). It can be clearly seen that E_{ex} increases systematically with x_f. Using a least-squares fit with linear regression analysis, the following relationship is obtained:

$$E_{\text{ex}}(x_f) = 5.2761 + 0.0209x_f\ \text{eV}. \tag{3}$$

To elucidate the isotope dependence of the band gap, the isotope dependence of the TO phonon energy $\hbar\omega_{\text{TO}}$ must be subtracted since it must be used in the CL process. In a harmonic approximation with the average atomic mass ($\overline{M}_f = 12 + x_f$) of the films, the isotope dependence of this TO mode should be given by $\hbar\omega_{\text{TO}}(x_f) = \hbar\omega_{\text{TO}}(0)\sqrt{12/\overline{M}_f}$ meV. This mode is known to have an energy of 141 ± 1 meV in natural abundance diamond.[27] However, as in the case of the Raman peak position shown in Fig. 1, the isotopic composition dependence of the phonon mode can deviate from this behavior due to the anharmonic effect and isotope disorder. In particular, the isotope disorder is known to play an important role.[17] Thus, the isotope composition dependence of $\hbar\omega_{\text{TO}}$ is computed using density functional perturbation theory,[28,29] including the effect of the isotope disorder. Here, a $2 \times 2 \times 2$ face-centered cubic (fcc) supercell with 16 carbon atoms is used to study nine different x_f value cases, $x_f = 0, \frac{2}{16}, \frac{4}{16}, \ldots, \frac{16}{16}$. By averaging the $\hbar\omega_{\text{TO}}$ values over all of the possible ^{12}C and ^{13}C configurations for each x_f, the TO-phonon mode energy for $\overline{M}_f$ is determined, as shown in Fig. 4. It is found that the data exhibits a convex downward curve, which agrees well with a previous calculation using a coherent potential approximation.[17] Fitting the data to a quadratic form, we obtain

$$\hbar\omega_{\text{TO}}(x_f) = 141.56 - 6.53x_f + 0.99x_f^2\ \text{meV}. \tag{4}$$

For a natural ^{13}C abundance of 1.1%, the phonon energy given by Eq. (4) agrees well with the experimental value of 141 ± 1 meV. Using Eq. (4), the difference between the calculated TO-phonon mode energy of ^{12}C ($x_f = 0$) and ^{13}C ($x_f = 1$) is

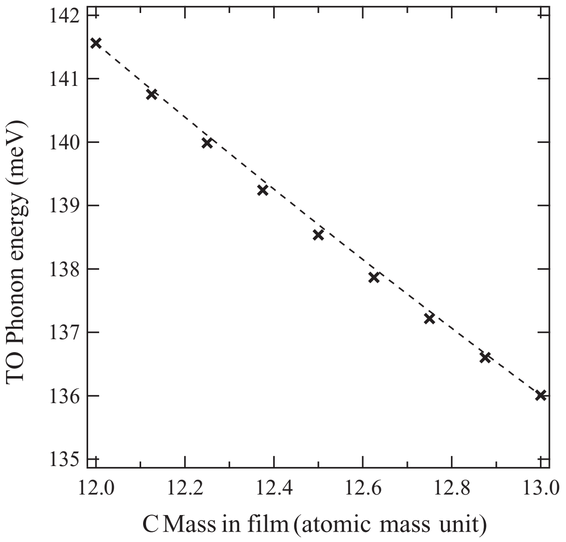

FIG. 4. TO phonon energy obtained from density functional perturbation theory, including the isotope disorder effect. The dashed line is a harmonic approximation calculation.

5.54 meV. Hence, the isotope composition dependence of the band-gap energy $E_g(x_f)$, due to isotopic substitution, is given by the following *quadratic* formula:

$$\begin{aligned} E_g(x_f) &= E_{\mathrm{ex}}(x_f) + E_x + \hbar\omega_{\mathrm{TO}}(x_f) \\ &= 5497.66 + 14.37x_f + 0.99x_f^2 \ \ \mathrm{meV}, \end{aligned} \tag{5}$$

where E_x is the FE$^{\mathrm{TO}}$ binding energy, having a value of 80 meV following the report by Dean *et al.*[27] Here, the exciton binding energy is considered to be unaffected by isotope substitution (see Supplemental Material in Ref. 30). From Eq. (5), it can be concluded that the maximum change of the band-gap energy due to substitution of ^{12}C by ^{13}C is $\Delta E_g \equiv E_g(0) - E_g(1) =$ 15.4 meV. This value is larger than all of the experimental values reported previously,[12,17,18] while it is in good agreement with the estimate of 16.5 ± 2.5 meV reported by Collins *et al.* using a zero-point renormalization obtained from a fit of the experimental temperature dependence of the band gap.[12]

It is interesting to note that this ΔE_g value should become even larger at room temperature. The temperature dependence of ΔE_g can be discussed through the temperature dependence of the band-gap renormalization due to electron-phonon interaction, $E_r(x_f,T) = E_g^0 - E_g(x_f,T)$, where E_g^0 is the band gap of the hypothetical system without lattice vibration, and its temperature dependence should be negligibly small. Since the primary contribution to $E_r(x_f,T)$ in isotopically pure monoatomic crystals should be proportional to $\overline{M}_f^{-1/2}$,[31] ΔE_g can be approximated as $\Delta E_g(T) = E_r(T)(1 - (12/13)^{1/2})$, where $E_r(T)$ denotes the band-gap renormalization of ^{12}C diamond, $E_r(0,T)$. From the experimental temperature dependence of the band gap in natural abundance diamond,[1] we can measure $\Delta E_r(T) = E_r(T) - E_r(T_0)$, where T_0 is the reference temperature (79 K in this work). Therefore, $\Delta E_g(T)$ is approximated by $\Delta E_g(T) - \Delta E_g(T_0) = (1 - [12/13]^{1/2})(E_r(T) - E_r(T_0))$ and $\Delta E_g(T = 79\ \mathrm{K}) =$ 15.4 meV. For example, at $T = 300$ K: $\Delta E_g(T = 300\ \mathrm{K}) \sim \Delta E_g(T = 79\ \mathrm{K}) + (1 - [12/13]^{1/2})(E_r(T) - E_r(T = 79\ \mathrm{K})) \approx 15.9$ meV, which is larger than the value at 79 K.

The large isotope effect on the electronic band gap observed in the present study is believed to be related to the fact that the homoepitaxial diamond films grown via microwave plasma-assisted CVD on pretreated single-crystal diamond have a low crystal defect density and low impurity incorporation. An additional point to be emphasized is that the full width at half maximum (FWHM) of the Raman peak of the nearly pure ^{12}C sample has been determined to be 1.5(5) cm^{-1} (Fig. 2). The broadening of the Raman peak can be related to a shortening of the phonon lifetime or phonon mean-free path due to the presence of lattice disorder in the crystal caused by an impurity. The FWHM of the Raman peak in perfect natural diamond is expected to be as low as 1.5 cm^{-1},[32,33] which is in good agreement with the present result obtained for CVD diamond film. In addition, since it is known that crystal strain affects the potentials of the valence band and the conduction band extrema, crystal imperfections due to impurities or defects may reduce the band gap, and consequently, the total exciton energy. The large isotope dependence of the band gap in these samples may be accompanied by a reduction in the internal stress associated with substitutional impurity atoms.

In conclusion, the isotope effect on the electronic band gap has been studied over a wide range of isotopic compositions of high-quality single-crystal CVD homoepitaxial diamond films grown using microwave plasma-assisted CVD. These high-quality diamond structures have revealed a significant change in the electronic band-gap energy upon isotope replacement. An isotope-dependent energy shift of the band gap, larger than those reported previously, was obtained. The present results update the formula for analyzing the electronic band gap in isotope composition-controlled diamond and for designing devices from a homojunction band engineering perspective, a very promising area of research in the future.[8,34]

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[*] Corresponding author: hideyuki-watanabe@aist.go.jp

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