Super-entropic Amorphous Diamond as Thermionic Energy Converters

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Amorphous diamond is essentially a chaotic carbon mixture with distorted sp^2 and sp^3 bonds. As such it possesses both metallic character of conductive graphite and semiconductor character of insulating diamond. Moreover, as each carbon atom is unique in its electronic state that is determined by the degree of distortion of its bonds, amorphous diamond contains numerous discrete potential energies for electrons. In fact, amorphous diamond may have the highest density of atoms (1.8×10^{23} per cubic centimeter) that is several times higher than ordinary materials (e.g. about four times of iron atoms or silicon atoms). Thus, amorphous diamond has the highest configuration entropy for both atoms and valence electrons.

Due to the distribution of discrete electronic energies with high density, amorphous diamond is uniquely capable to generate electricity and emit radiation. It has been demonstrated that amorphous diamond can be made as silicon free solar cells, front panel display field emission source, sensitive thermal sensing by IR detection, and perfect black body for energy conversion. Various amorphous diamond devices are being fabricated to exploit the superb properties of amorphous diamond.

***Keywords**: amorphous diamond, field emission, black body, front panel display, infrared detection, super entropy*

1. The Polluted Solar Cells Made of Crystalline Silicon

The mainstream solar cells are made of crystalline silicon. Although the cost for generating one KwH is 5-10 times of conventional fuel fossil power plants, crystalline silicon solar cells are thought to be environmentally friendly. However, crystalline silicon is typically produced from highly pure quartz that may be extracted from beach sand. The fact that white beach sand can only be produced after tens of million years weathering and washing implies that quartz is very stable. Consequently, it would require very high temperature (e.g. 1700℃ to reduce quartz to form metallurgical grade silicon. While silicon is reduced, 1.5 time of carbon dioxide is released that contributes to the green house effect. Moreover, the metallurgical grade silicon must be purified, again at high temperature. Eventually, the pure silicon is melted above 1410℃) to form either ingot for single crystal or casting for polycrystals. In all these high temperature process steps, high amount of electricity may be needed.

The crystalline silicon for making solar cells once get to a price tag of about $100/Kg. For making solar cells, about 0.5 mm thick, including cutting kerf, may be needed, so one kilogram of silicon may produce about 1 m^2 to exposed under sun. As the solar constant is about 1 Kw/m^2, and the average total efficiency one day of silicon solar cells as measured around the clock is less than 10%, we may expect that the power for one kilogram silicon material is about 0.1 Kw. Assuming that the power cost is about $0.05/KwH, the above 0.1 Kw solar panel would require about 2000 KwH or energy to produce. To pay back the bill, the silicon solar cells may have to run 20,000 hours or about 2.3 years! During this period, the governments have to subsidize the inefficiency of the electricity produced by such pollution causing silicon. Consequently, it is desirable to constructing solar cells by using more environmental friendly materials. One of such materials is amorphous diamond.

2. Super-entropic Material

Amorphous diamond appears to be contradictory term, like liquid crystal or glassy metal. Amorphous means non-crystalline and diamond implies crystalline. However, this terminology is meaningful because unlike silicon that forms only sp^3 bonds, i.e. diamond structure, carbon may form either sp^2 (graphitic) or sp^3 (diamond) bond. Although there is one form of amorphous silicon, there can be at least two forms of amorphous carbon, so amorphous diamond can be distinguished from amorphous graphite, and together they are amorphous carbon.

Amorphous diamond is formally known as tetrahedral amorphous carbon (tac), it is really a diamond-like carbon (DLC) that contains no non-carbon impurities (e.g. H). Amorphous diamond is essentially a chaotic carbon mixture with distorted sp^2 and sp^3 bonds. As such it possesses both metallic character of conductive graphite and semiconductor character of insulating diamond. Moreover, as each carbon atom is unique in its electronic state that is determined by the degree of distortion of its bonds. Hence, amorphous diamond contains numerous discrete potential energy for electrons. In fact, amorphous diamond may have the highest density of atomic occupancy (1.8×10^{23} per cubic centimeter) that is several times higher than ordinary materials (e.g. about four times of iron atoms or silicon atoms). Thus, amorphous diamond has the highest configuration entropy for both atoms and valence electrons.

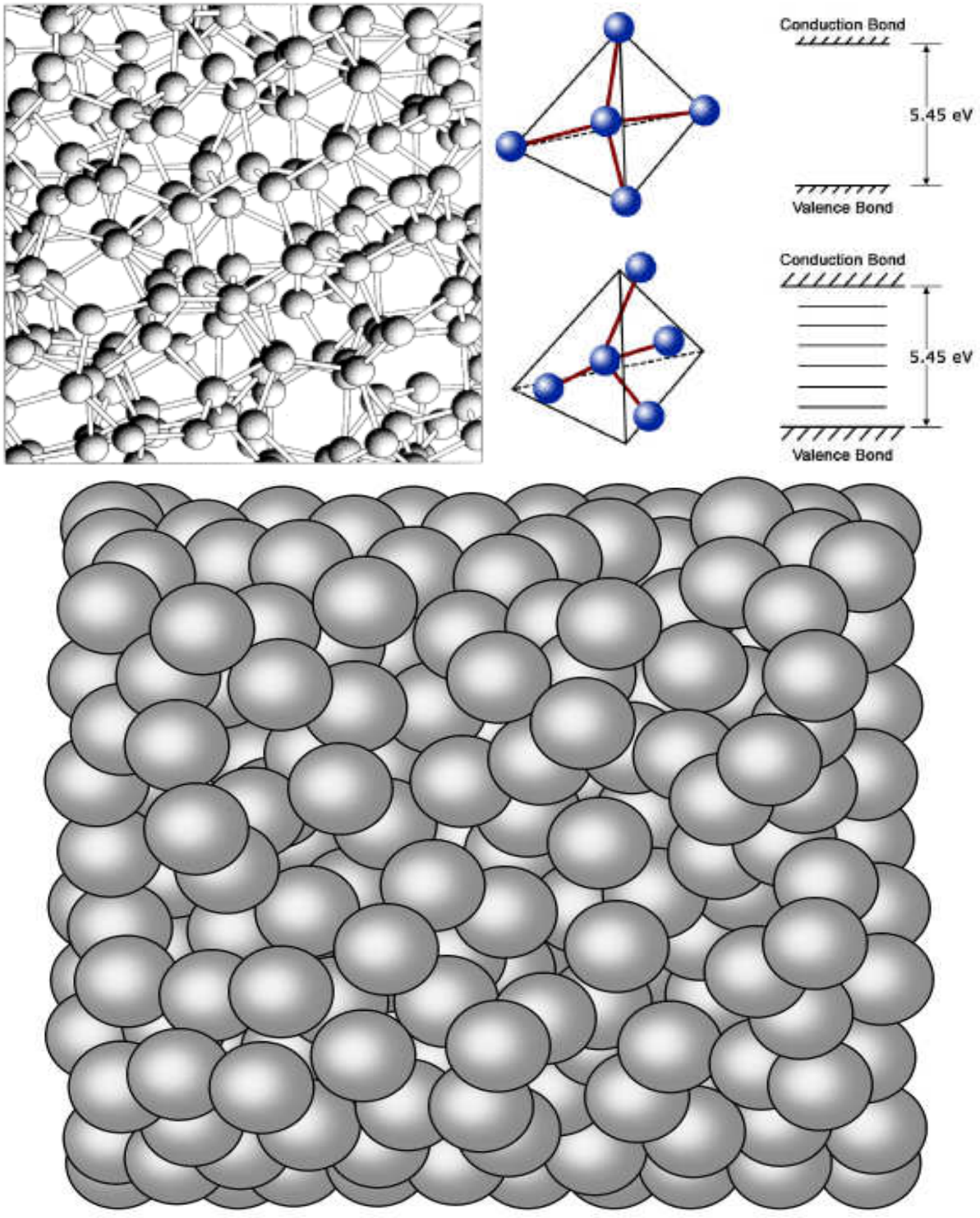

Fig. 1: The high atomic density and the unique way of distorting bonds for each atom makes amorphous diamond the material with the highest configurational entropy. As a result, amorphous diamond has the densest electron states that are discrete. This is in contrast of all materials that have either overlapped electron orbitals, as in the case of metal, or few discrete electron states, as in the case of semiconductors or insulators.

Amorphous diamond can be conveniently deposited by PVD methods, such as by sputtering or arc depositions. Due to the low temperature (<150℃) of deposition, amorphous diamond can be coated on most materials including metal, semiconductor, or even polymers. This flexibility makes amorphous diamond useful for many applications.

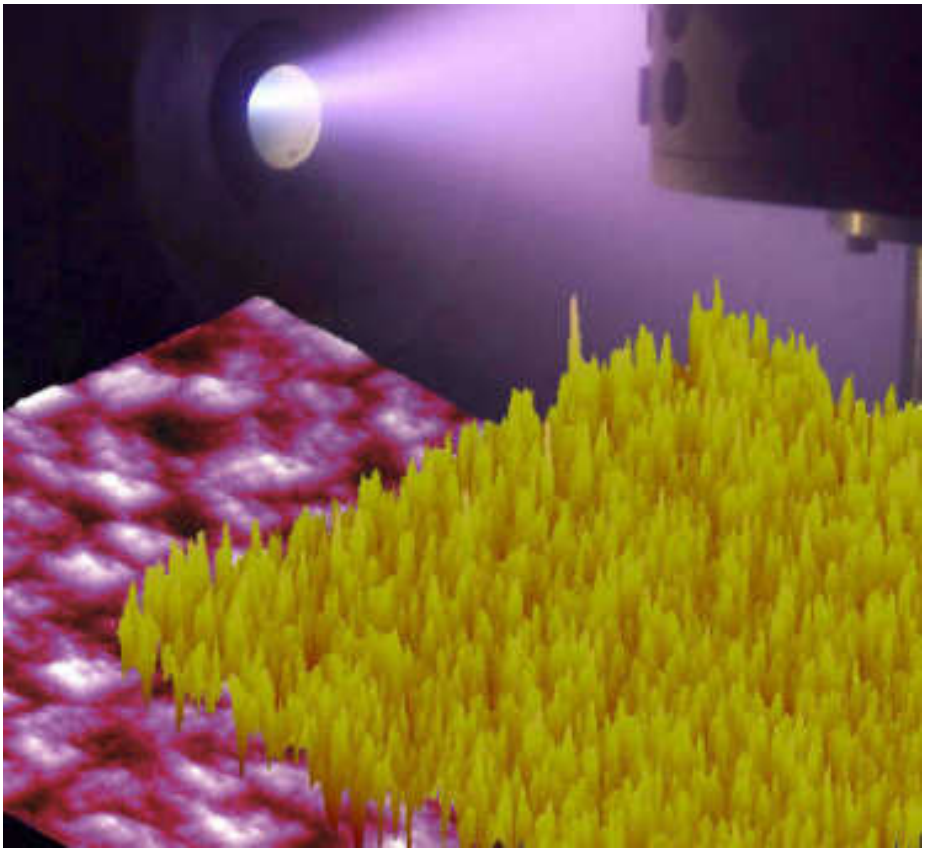

Fig. 2: Amorphous diamond can be coated on substrates by cathodic arc process. In this case, the surface smoothness can be adjusted by the arc current; and the material properties (e.g. sp^3/sp^2 ratio of the carbon atoms), by the bias on the substrate.

Due to such high configuration entropy of valence electrons, amorphous diamond is capable to advance electron energy by absorbing small increments of energy, such as by converting thermal energy (lattice vibration) to potential energy (electron state). If amorphous diamond is exposed in high vacuum (e.g. 10^{-6} torr), the energy state may be higher than vacuum state so amorphous diamond my emit electrons simply by heating. Because amorphous diamond has the highest discrete electronic states, it is the most thermionic material known.

3. Low Work Function

In general, materials fall in three camps, conductor, semiconductor and insulator, amorphous diamond is an atomistic mixture of all, so electrons can pass through it and be emitted in vacuum. By contrast, all other materials will stop electrons either inside the crystal lattice (e.g. an insulator) or on the surface (e.g. a conductor). The unique ability for amorphous diamond to emit electrons in vacuum by receiving low levels of energy makes it the excellent of field emitter with very low apparent work function. Amorphous diamond can be coated on metallic substrate by cathodic arc process to become a useful field emitter in vacuum.

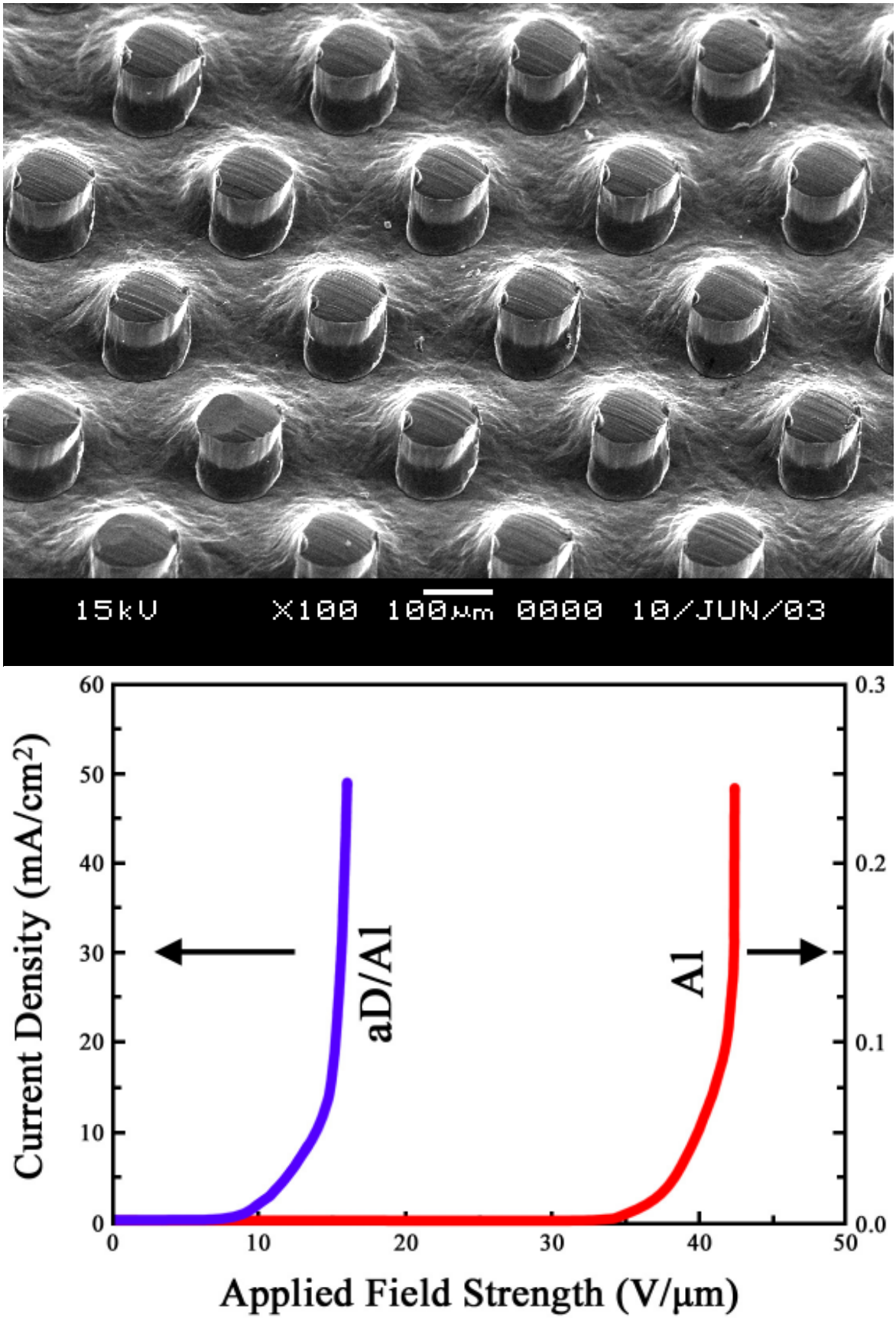

Fig. 3: The dramatic enhancement of emission current by coating amorphous diamond on aluminum cathode with bumps.

4. Thermionic Emission

Even without high vacuum, amorphous diamond coated nickel electrodes of cold cathode fluorescent lamps (CCFL) used for back lighting can reduce significantly the turn-on voltage.

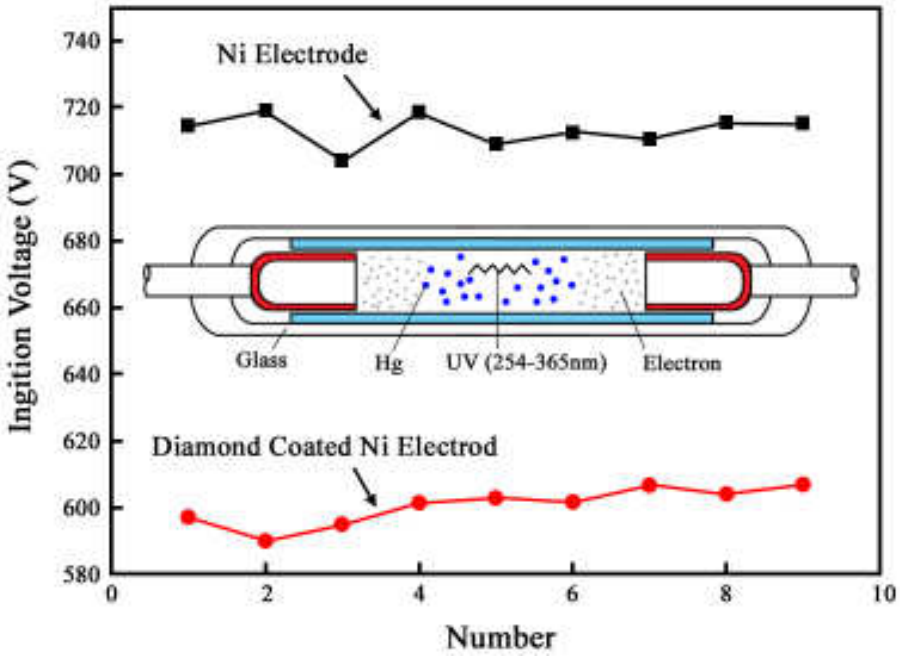

Fig. 4: The reduction of ignition voltage of CCFL by coating nickel electrodes with amorphous diamond.

Due to its exceptional ability to increase the potential energy of electrons by absorbing heat, amorphous diamond coated metal is highly thermionic.

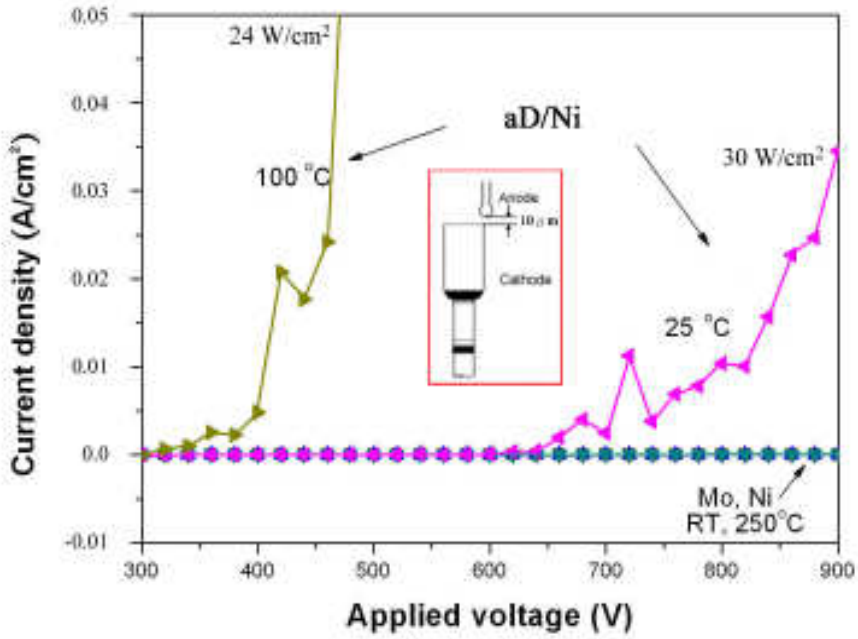

Fig. 5: The great enhancement of emitted current from amorphous diamond coated nickel electrode in CCFL by modest heating.

Based on the above thermionic effect, the effective work function, i.e. the activation energy for electron emission in vacuum, can be lower than 1 eV. This is the lowest of all materials that have effective work function higher than 2 eV. Due to this unique thermionic character, amorphous diamond can emit more current than even carbon nanotubes (CNT) that have a high work function, but with a nanometer radius to enhance the electrical field. Moreover, as amorphous diamond is solid in content, it can emit electrons at a much lower temperature than CNT that will concentrate electricity on the skin of the hallow structure. In fact, the skin of each CNT will burn out when the current exceeds 20 μA. As a result, CNT devices are not reliable (e.g. Samsung's CNT front panel display or Iljin's CNT backlight). In contrast, amorphous diamond field emission can be highly robust. This is particularly suited for display or backlight applications.

5. Field Emission Display

The sensitive field emission and thermionic enhancement of amorphous diamond would make it an ideal coating material for Spindt (metal spikes) array that may be used for front panel displays. Such field emission displays will have the lowest operational power and panel temperature.

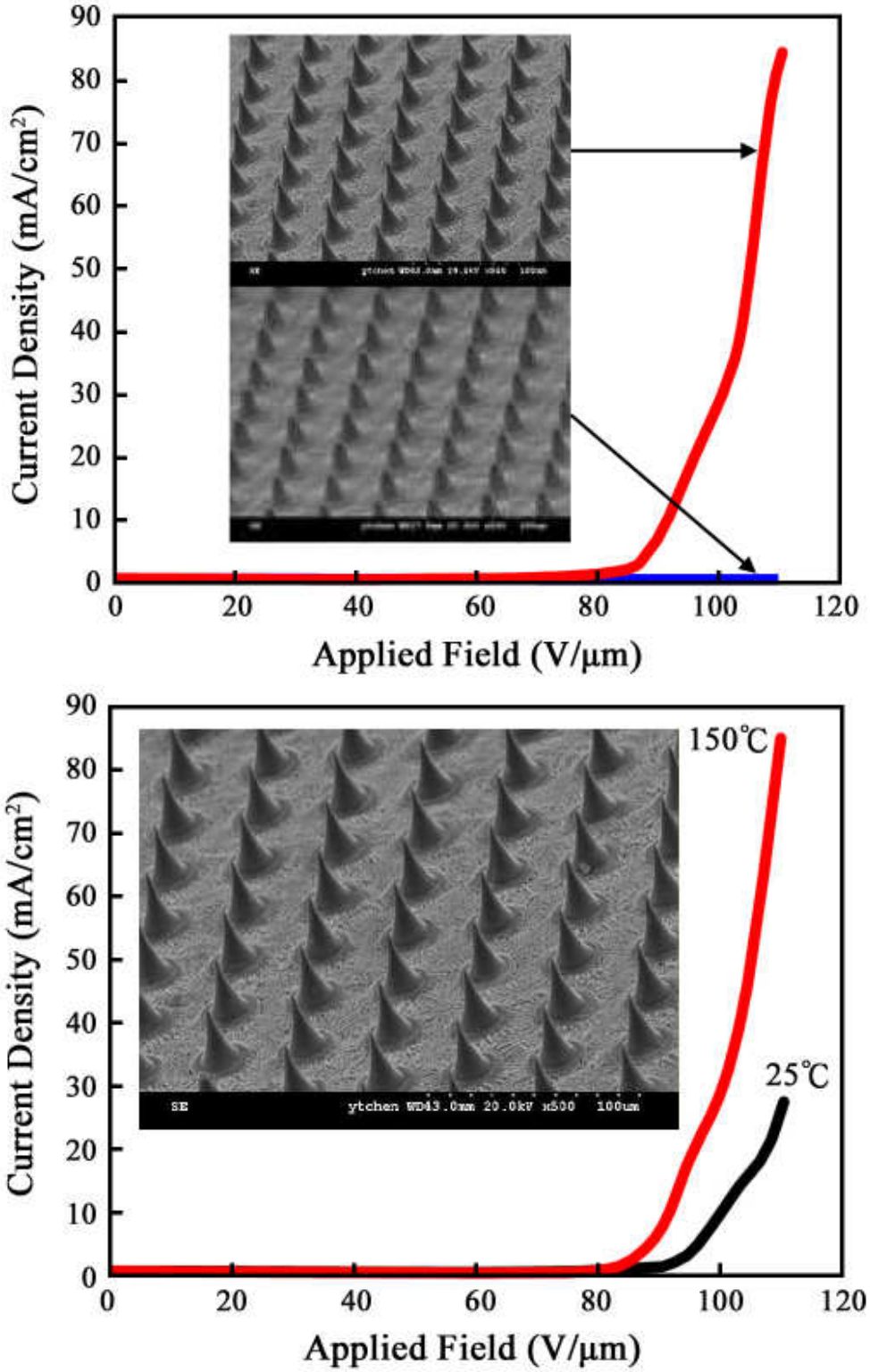

Fig. 6: The field emission of amorphous diamond coated nickel alloy cones can be enhanced by either sharpening the cone tips (upper diagram) or by modest heating (lower diagram).

By coating amorphous diamond on arrays of Spindt cones that are controlled by the cross bars of electrodes, the emission of a particular addressed pixel can be triggered to excite phosphor of RBG colors. Such a device can be used as field emission display for TV and other devices.

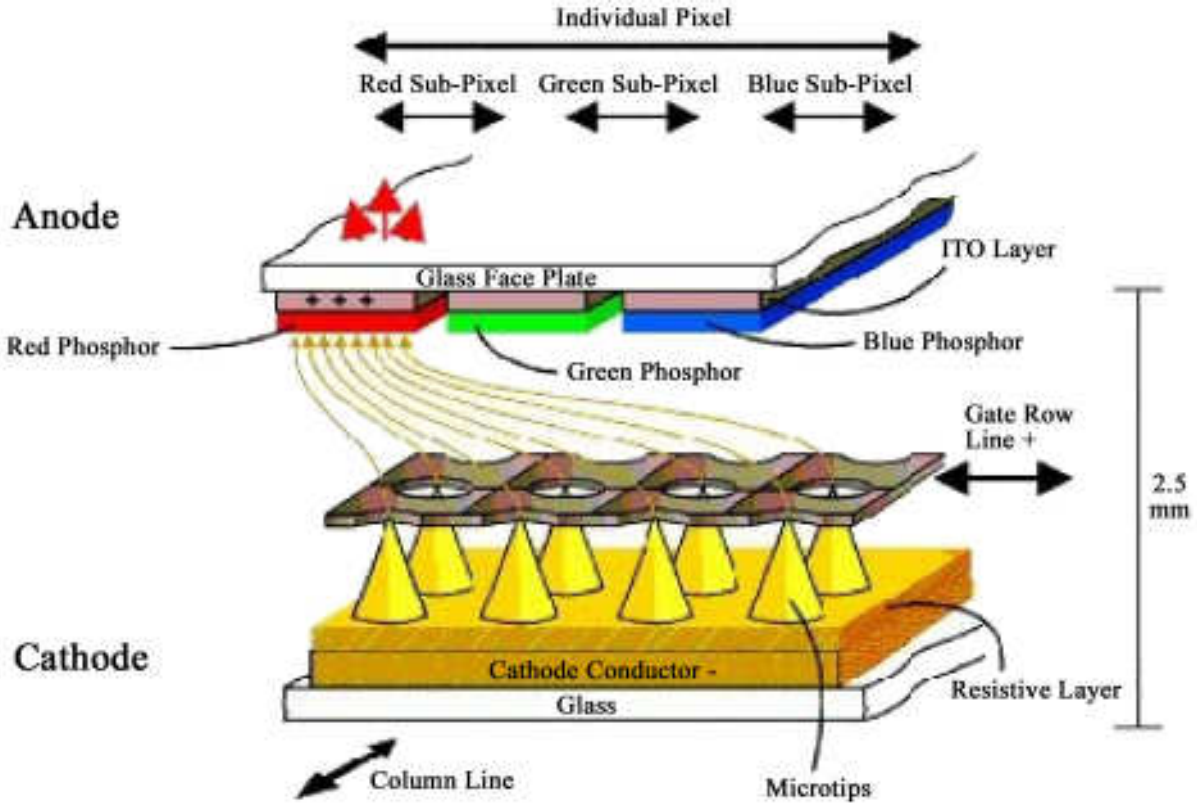

Fig. 7: The schematic of front panel display using amorphous diamond coated micro tips of metal cones.

6. Black Body Radiator

Materials fall under two camps: electrical conductors (metals) can conduct heat (phonon), but not emit heat (IR), and electrical insulators (ceramics) are just the opposite. However, amorphous diamond is both the thermal conductor and thermal emitter. Amorphous diamond is not only thermionic, it is also the perfect black body. Typically a metal has a low emissivity (e.g. 2%), but an insulator has a poor thermal conductance (e.g. 10 W/mK), so both of them cannot sustain the emission far infrared from a warm surface. However, amorphous diamond has a thermal conductivity (about 500 W/mK) that is even higher than the best metal (420 W/mK for silver), and its emissivity is nearly 100%. It was measured that at a temperature as low as 70℃, the sustained heat emission was 0.088 W/cm^2, this equals to what predicted by Stefan-Boltzmann's equation (5.67×10^{-8} T[K]^4/m^2) for black body. This implies that amorphous diamond has an emissivity of about 100% and the emission is not limited by its thermal conductivity. The exceptional ability to emit heat makes amorphous diamond an excellent thermal radiator for cooling high-powered LED.

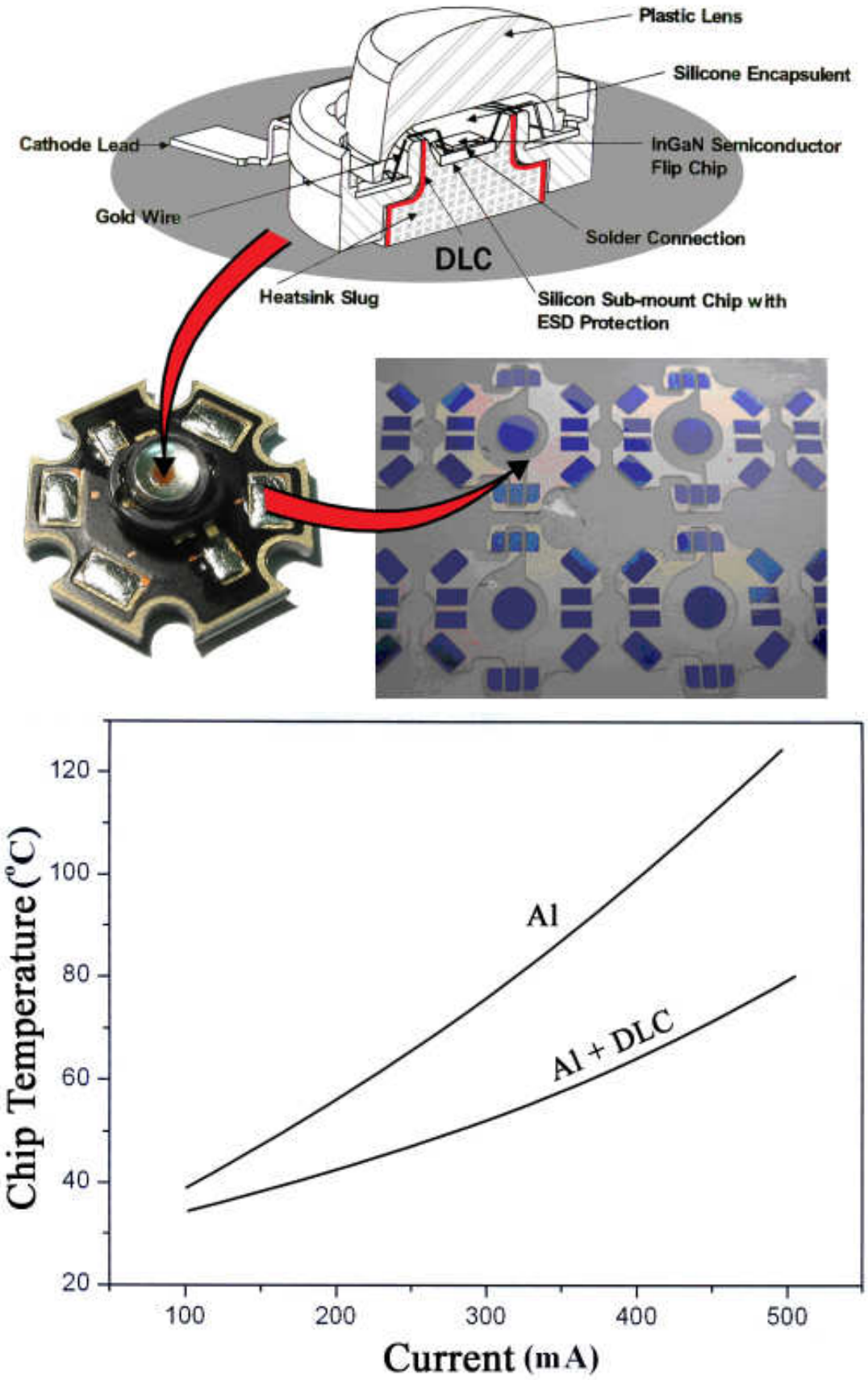

Fig. 8: The cooling of LED junction temperature by coating amorphous diamond on the surface of its aluminum substrate heat spreader.

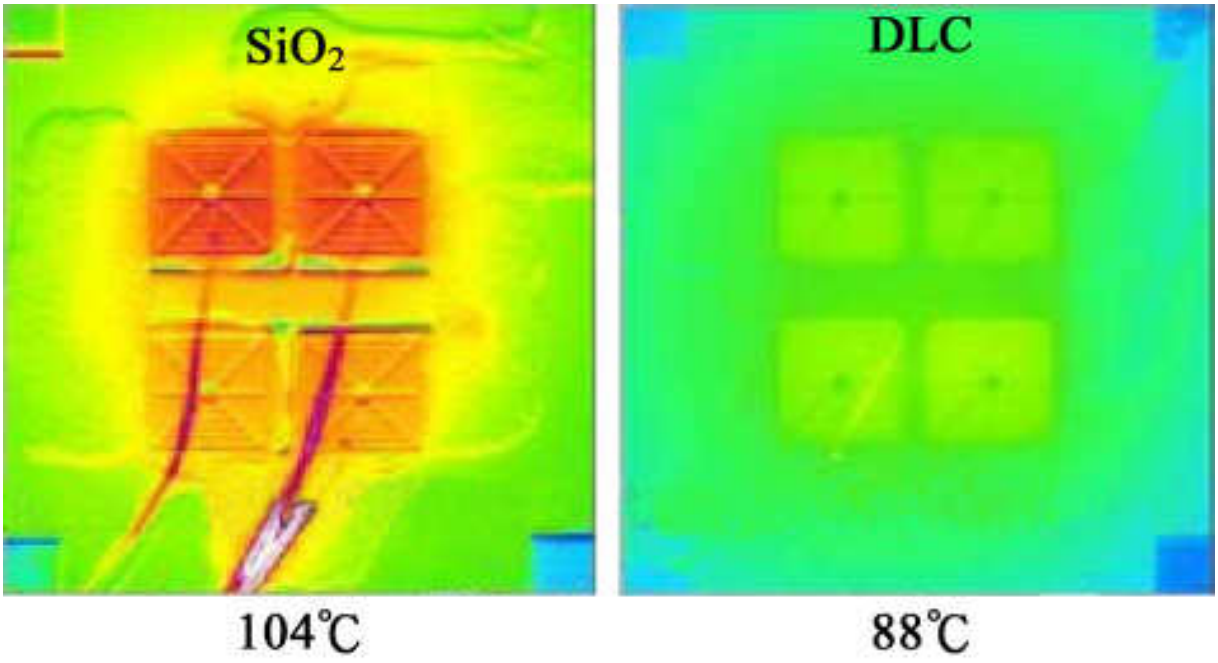

Fig. 9: The dramatic cooling effect of high bright LED that was operated at 350 mA by replacing the oxidized layer of the silicon submount with DLC coating.

As the black body is reversible, amorphous diamond can be used as the heat absorber for applications related to advanced thermal imaging of infrared source or mundane water heating by absorbing sunlight.

7. DLC Eletro-Luminescence (DEL)

Amorphous diamond coated PET, replacing silver grease, was used as the electrode for the light panel based on electro-luminescence. The result indicated that the brightness of the phosphors increased substantially than conventional EL. Moreover, the decay rate of the illumination was greatly reduced (Sea-Fue Wang, personal communications). In a previous study, the brightness of DEL was shown to increase linearly with the increase of the applied voltage, frequency of the alternative current, and the increase of temperature. The improvement of DEL over EL was like due to the increased voltage in amorphous diamond compared to metal conductor under the same externally applied electrical field.

Because amorphous diamond electrons are bound loosely, they can be free with the input of low amount of energy (e.g. external filed). Consequently, under the external field of alternative current, higher concentration of electrons could be generated momentarily. The fast accumulation of free electrons in amorphous diamond was demonstrated in the rapid saturation of electrons when an external bias of direct current was applied. This phenomenon made amorphous diamond highly useful as the energy storage device (e.g. a high density capacitor). The enhanced capacitance on amorphous diamond apparently made the DEL brighter than EL that used metal conductors. Because the electrical current was not increased in DEL, the likelihood of thermal damage due to the local current concentration of electricity on phosphor particles can be reduced. This explained why DEL's light faded away much slower than conventional EL devices. EL is a low cost illuminator that can be applied to large area. Unfortunately, its brightness has been low (e.g. <3000 cd/m^2), and the service life has been low (e.g. 2000 hours). DEL can overcome the limitation of EL, and hence it can be an alternative to backlighting or for generally illumination.

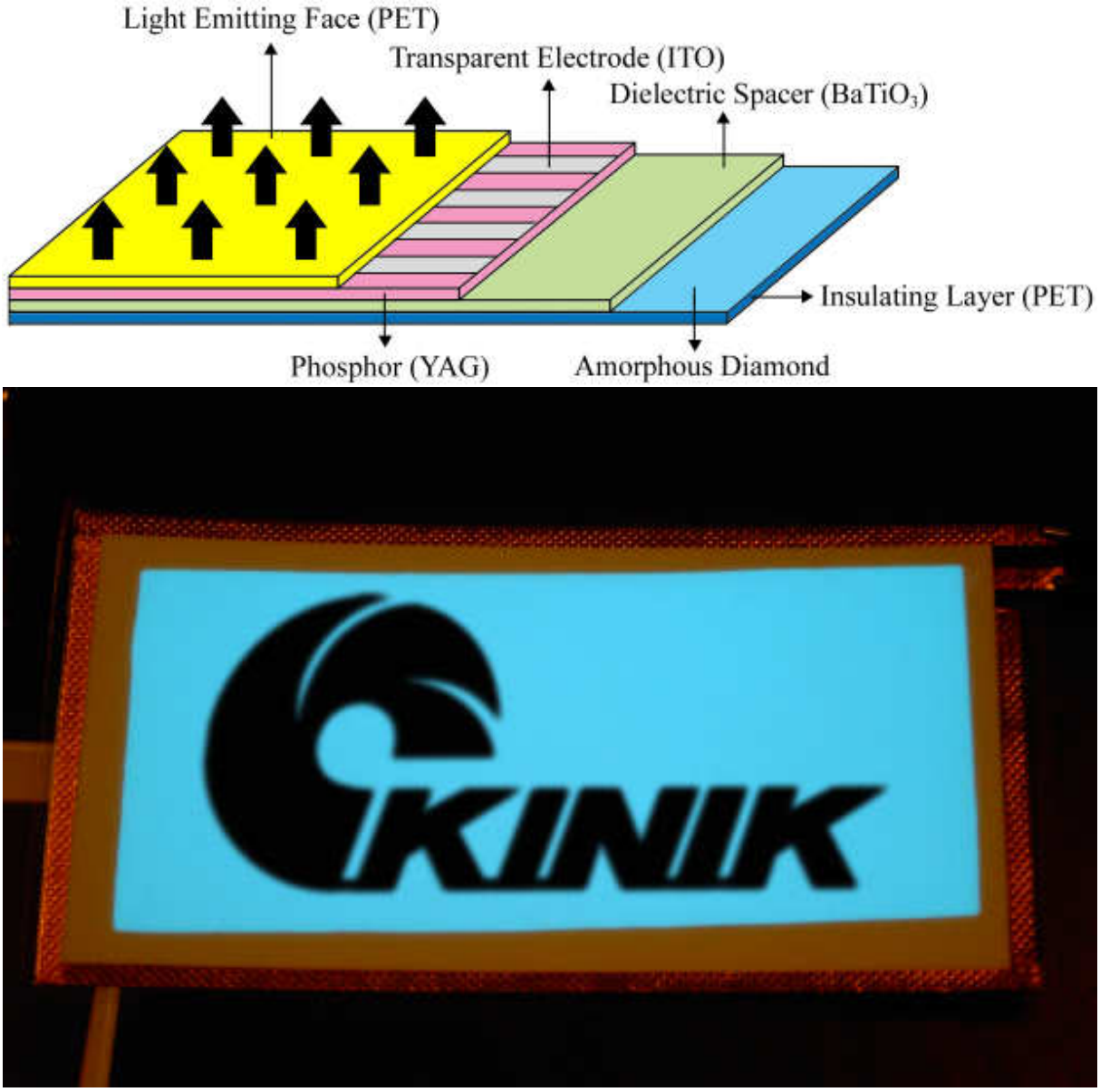

Fig. 10: The schematic of DEL design and the brightness of DEL panel (A4 size).

8. Amorphous Diamond Solar Cell

The merit of amorphous diamond to convert either light or heat to electricity can be applied to solar cell panels or thermal electrical generators. For example, amorphous diamond was over covered coated on indium tin oxide (ITO), the transparent electrical conductor that was coated on a glass substrate. This panel was separated from another ITO coated glass by glass bead spacer. The gap was sealed around and the space was pumped down to high vacuum (10^{-6} torr). This panel was exposed to a xenon light that irradiated a spectrum with an energy output similar to solar constant (AM1.0 or $0.1W/cm^2$). An external bias was applied and the electric current was monitored. It was demonstrated that the current increased substantially when light shone through or when amorphous diamond was heated up.

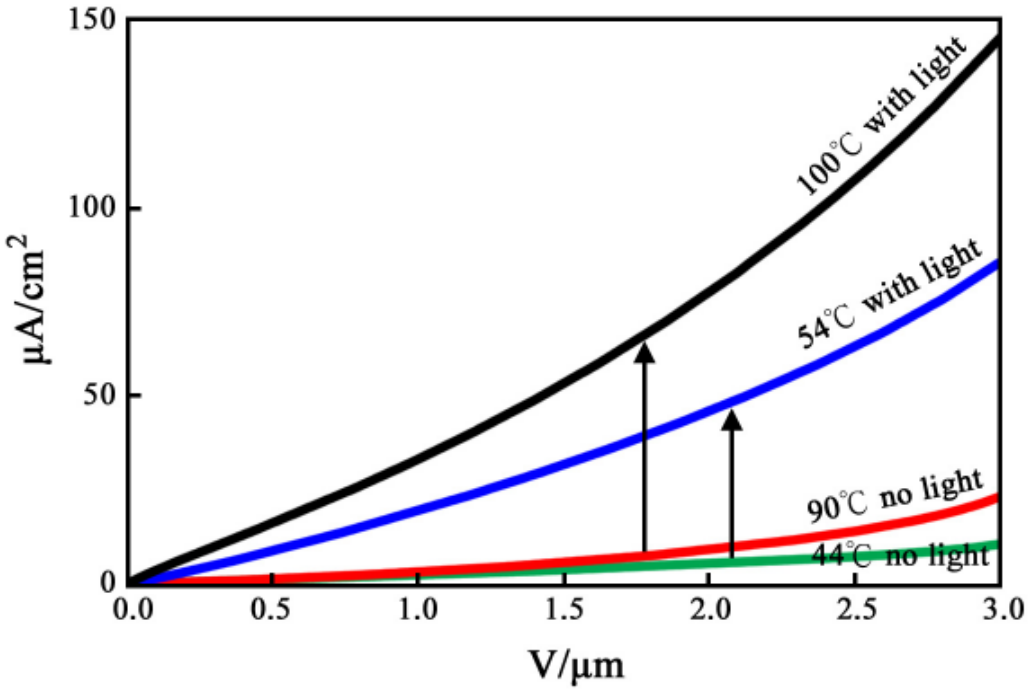

Fig. 11: Amorphous diamond can enhance electron emission in vacuum by light absorption and by thermal agitation.

When the applied bias was gradually reduced to zero, the current enhanced by xenon lamp was not dependent on the bias. Hence, the field emission could be triggered by sunshine directly without adding an external bias. However, the current density was too low to be useful as a solar panel unless the vacuum gap could be reduced further from 7 microns.

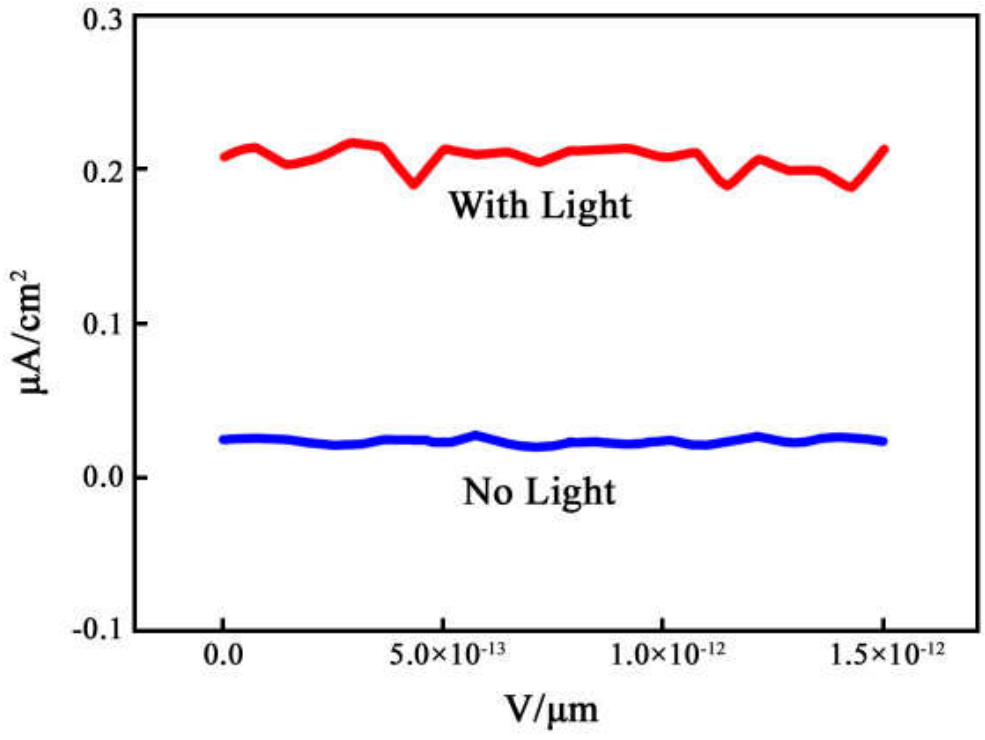

Fig. 12: The field emission became spontaneous when the external bias was reduced to zero.

When the vacuum was back filled with iodine, the current could be generated noticeably without applying the external field. This current was further increased by sensitizing amorphous diamond with a light absorbent dye. But even so, it was still low with the conversion efficiency.

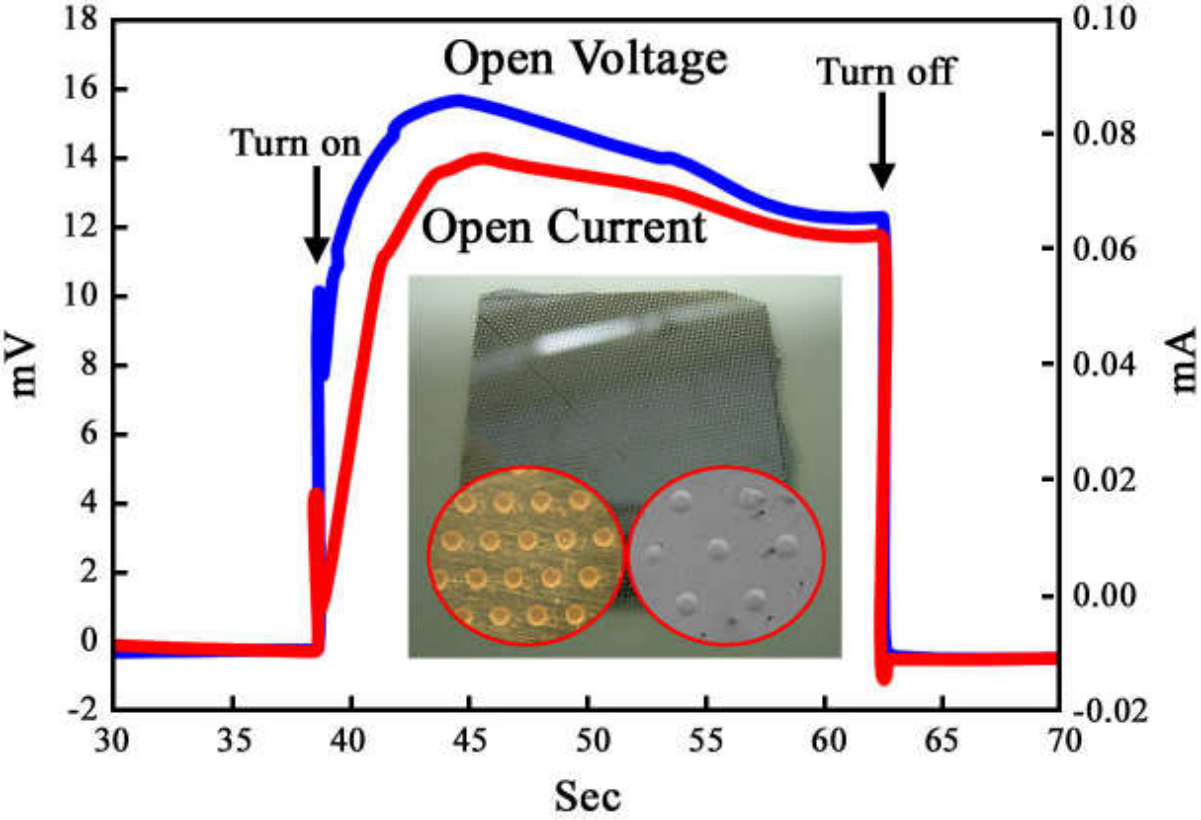

Fig. 13: The photo-electric effect of amorphous diamond when exposed to a xenon lamp (AM1.0) of about 0.1 W/cm^2. In the experiment, the vacuum gap was back filled with liquid electrolyte of iodine.

The amorphous diamond solar cell was also constructed with a silicon layer in a hybrid design. In this case, no vacuum was needed. In one example, the nitrogen doped amorphous diamond was coated on boron doped silicon substrate. This hybrid design showed a dramatic increase in photo electricity, much higher than using a vacuum gap or back filed with a liquid electrolyte.

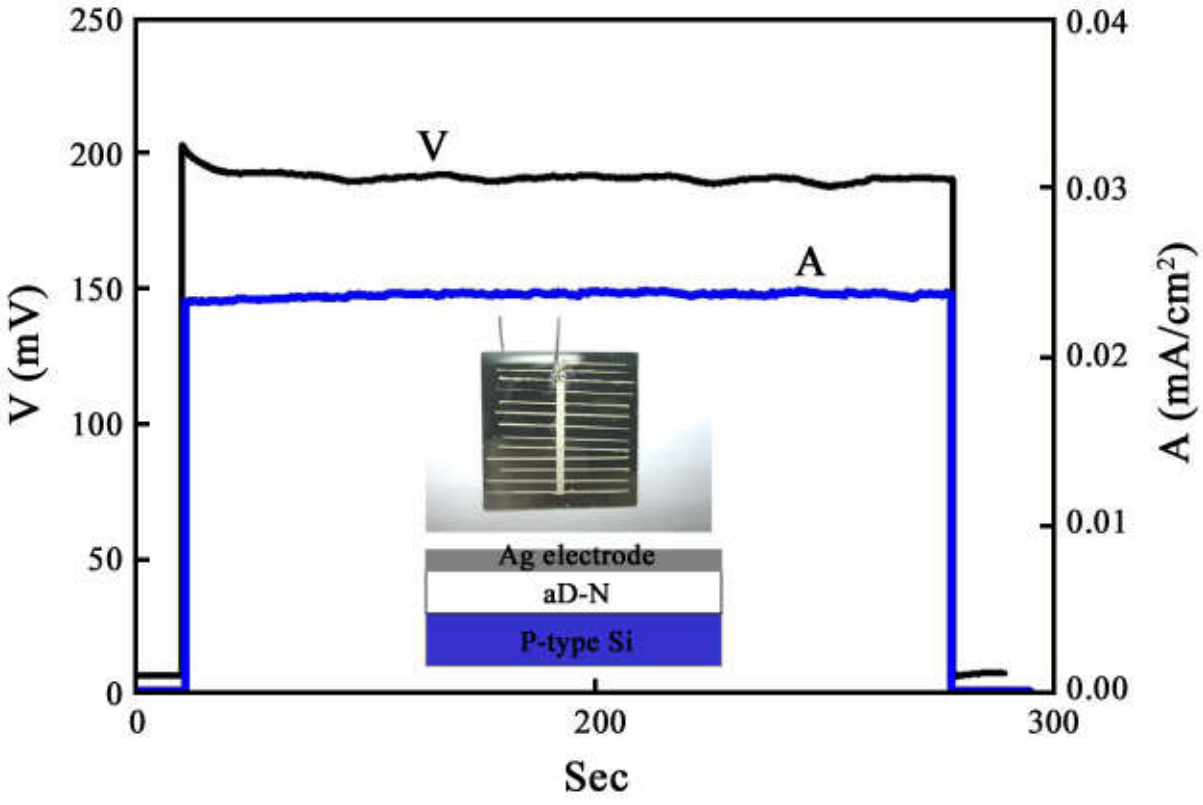

Fig. 14: The photo electric effect of nitrogen doped amorphous diamond coated on boron doped silicon layer.

When a monochrometer was used to filter the broad spectrum of the xenon lamp and the photocurrents of amorphous diamond coated silicon and silicon solar cell were measured and compared, the former exhibited a much higher value. Upon cooling the semiconductors to a cryogenic temperature of liquid nitrogen (70 K), the electrical current generated by light increased. Moreover, the increase was higher with shorter wavelengths (i.e. with higher energy). However, amorphous diamond coated silicon showed much higher cooling enhancement and also the blue shift of the peak wavelength.

The above observation demonstrated that amorphous diamond could absorb light and generate electricity more effectively than silicon. This is particularly attractive as amorphous diamond is radiation superhard and it would not be susceptible to UV damage. Amorphous silicon solar cells have the advantages of thin film and low cost, but the aging problem of UV damage makes it less useful so more costly crystalline silicon plates are used as solar panels. It would appear that amorphous diamond coating of amorphous silicon solar cells can boost both the energy conversion efficiency and the longevity of the service.

Due to the high electric resistance of amorphous diamond, the electric current it generated was dissipated as heat so the final output of electricity was significantly reduced. The dampening effect was greatly reduced by cooling the device at liquid nitrogen temperature. However, alternative methods by channeling out electricity rapidly once it is formed may also be effective to preserve the electricity generated. One example is to coat amorphous diamond on amorphous silicon layers and stack them together. Due to the thinness (e.g. 100 nm) of the amorphous diamond and amorphous silicon, the light absorbed by each layer can generate electricity independently. The electricity can then be channeled out readily due to the short distance of travel to reach the electrode. The combined electricity would retain most of the energy derived from sunlight.

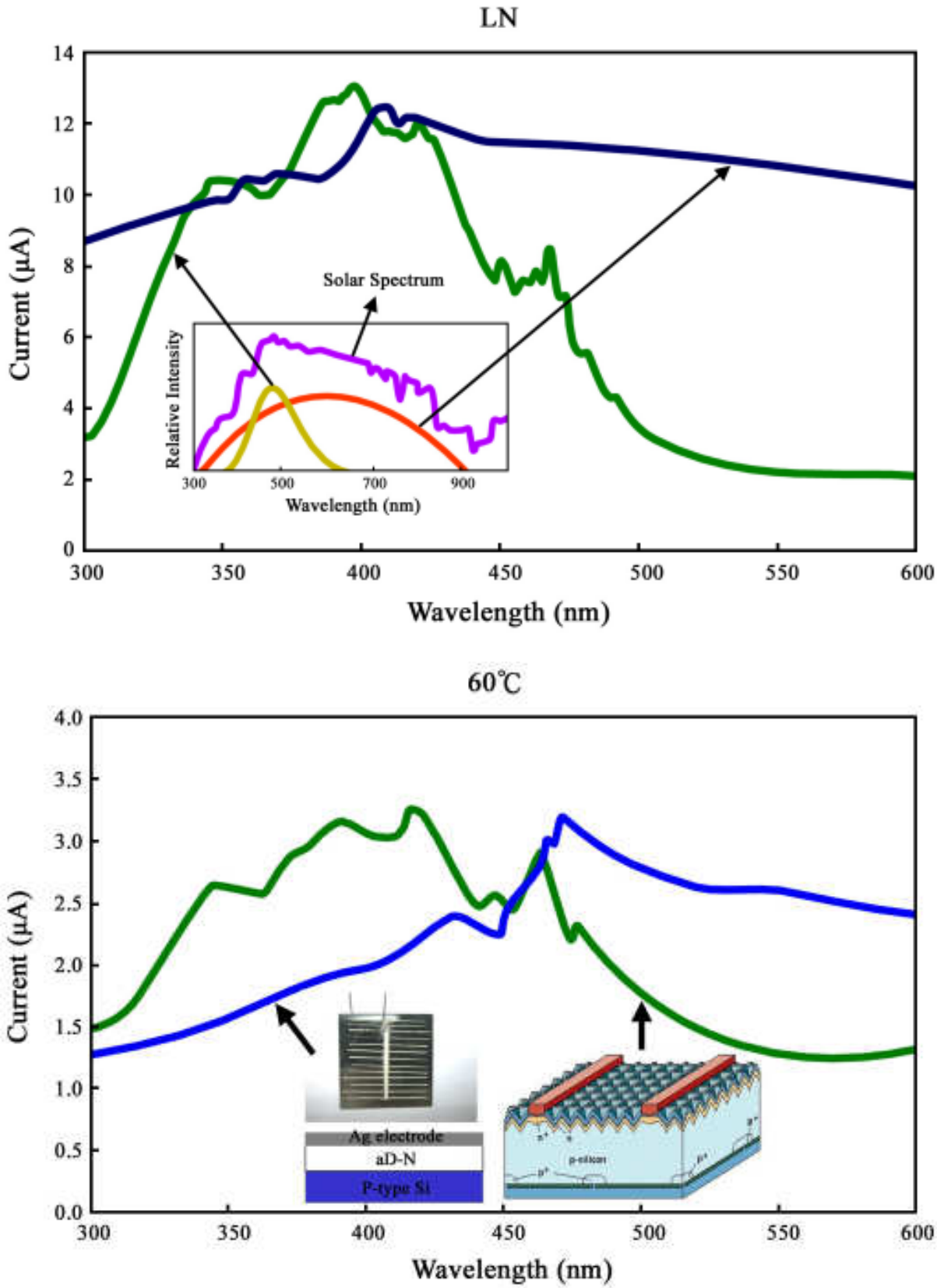

Fig. 15: The photo electrical current as a function of optical wavelength. Note that amorphous diamond could convert more current with IR irradiation than pure silicon. Moreover, the cooling enhancement of both energy and intensity was more obvious.

In summary, amorphous diamond has the highest density of discrete electronic states. This

unique feature makes amorphous diamond particularly useful as energy converters, such as field emitters, solar cells, thermal generators, radiation coolers, and heat absorbers.

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