Cold Cathode Fluorescence Light with Amorphous Diamond Coated Electrodes

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ABSTRACT

Amorphous diamond is the only material that can emit electrons in vacuum when applied with an electrical field of only a few volts per micron and such current can increase hundreds or millions times when heated to only a few hundreds degrees centigrade. This miracle is due to amorphous diamond's extreme atomic structure, with the highest atomic density and the largest configurational entropy. Amorphous diamond is made of carbon atoms with electrical resistivity that ranges from graphitic conductor to diamond-like insulator. But unlike ordinary composite materials that contain domains of relatively uniform material (e.g. metal and ceramic), each carbon atom in the amorphous diamond is unique in electronic bonding and energy state. In fact, amorphous diamond can be viewed as a self doped variable conductor. In comparison, semiconductors are chemically doped crystalline material. The numerous energy states in amorphous diamond can allow electrons to possess discrete energies so the inputted energy can be absorbed with a wide spectrum. Hence, even with the thermal energy may be absorbed to increase the energy of electrons. As a result, amorphous diamond can be a thermal generator, such as that for a solar cell. In this case, the energy conversion can have much higher efficiency (e.g. 50%) than that (e.g. 15%) of silicon based solar cells that can absorb only a narrow spectrum of sun light. As a solar cell, amorphous diamond has another advantage that its radiation hardness is the highest of all materials, hence, its thermal electricity efficiency will not attenuate as does the photo electrical semiconductor based solar cells.

An immediate application of amorphous diamond is to coat it on electron emitting electrodes, such as that used as cold cathode fluorescence lamps (CCFL) that illuminate liquid crystal displays (LCD), such is that used on note books and television sets. Amorphous diamond can dramatically reduce the voltage used to lit CCFL so the lamp life can be greatly extended. Moreover, the electrical current can be simultaneously increased to enhance the brightness of the light.

Keywords: amorphous diamond, solar cell, diamond electrode, thermal radiation, heat spreader, electroluminescence

1 ULTRA ENTROPY MATERIAL [2-6]

Electrons are unstable in vacuum so they can be bound to atoms. The more stable is the electrons in the atom, the more difficult for them to leave the atom and drift away in vacuum. For an electron to emit from an electrode, the energy of the electron must be increased so it can approach the vacuum energy of an electron. In metals, electron energy can be at any level as the conductive band is continuous. However, if external energy (e.g. heat) is not available, the energy of an electron will soon lose and assume the lowest level energy, i.e. the ground state. As the thermal energy is very small relative to the vacuum energy, even when the metal is heated to 1000 °C, its thermal energy is only about 0.1 eV that is only a few percent needed to overcome the activation energy. Consequently, electrons in a metal electrode cannot be emitted unless a very high voltage is applied. This is the problem metal electrodes is facing with CCFL.

In the case of applying a diamond film, electrons can take a higher energy level above the ground state and perch there for an indefinite period of time. This activated electron can be driven to vacuum with a much lower voltage. Once it is off the diamond surface, another electron can assume the same energy level so a stream of electrons can be emitted at a lower voltage. This lower voltage of emission was what Hitachi discovered with their diamond film coated CCFL.

However, a diamond film contains only very few discrete energy levels above the ground state, each discrete level is created by an atom that is not in the crystal lattice inequilibrium, such as a boron doped atom, or a carbon atom in stress. As there are few such discrete energy levels, so the voltage to move electrons along the "energy ladder" is still high. In order to further lower the gap of "energy rungs," more atoms in diamond must be in stress. The extreme of such stressed diamond film is called diamond-like carbon (DLC). In the case of the ideal DLC, the electron in every carbon atom is distinct so the discrete energy levels can be numerous. This is the structure for the lowest possible voltage that is required to emit electrons in a CCFL.

Carbon can take the form of metallic graphite with triangular sp² bonds, or insulating diamond with tetrahedral sp³ bonds. Amorphous diamond is diamond-like carbon

(DLC) that is joined together by distorted tetrahedral bonds. The distortion will increase the energy of the bonding electron and decrease the band gap. Because there are numerous ways of distorting tetrahedral bonds, each carbon atom in amorphous atom will have different band gaps. In essence, amorphous diamond is self-doped or physically doped multiple "semiconductors" that are distinguished from conventional foreign doped or chemically doped semiconductors.

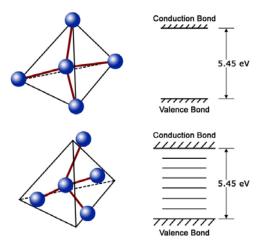


Figure 1: The symmetrical tetrahedral coordination of carbon atoms in diamond can form a wide band gap (top diagram), but the distorted tetrahedral coordination of carbon atoms in amorphous diamond will incorporate an energy ladder to allow electrons to increase energy by receiving small incremental thermal (phonon) energy.

Amorphous diamond may be viewed as super-cooled liquid diamond. As such, it possesses the highest atomic (not mass or occupancy) density (about 2 x 10²³/cm³) of all materials. Unlike ordinary materials with their crystal structures loosened up upon melting, the molten diamond is actually denser than even the crystalline diamond. Hence, amorphous diamond has more atoms per unit volume than diamond that has the highest atomic density (about 1.76 \times 10²³/cm³) of all materials. Because each atom is at a different energy state, amorphous diamond has by far the most discrete energy levels of electrons for all materials. The energy states of amorphous diamond spans from metallic graphite to insulating diamond, hence amorphous diamond can absorb sun light with a wide range of photon energies. On the bright daylight, the solar power (solar constant) is about 1000W/m², for a typical semiconductor solar cell, the average retrievable power is about 150 W/m², as the rest energy is reflected, transmitted, or becoming heat. In the case of amorphous diamond, it can pick up almost all magnitudes of solar energies. Moreover, the absorbed radiation energy can accumulate by climbing the above described energy ladder to drive electrons to form a continuous stream of electricity. In this case, the theoretical conversion power can be as high as 600 W/m²!

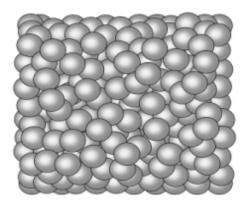


Figure 2: Amorphous diamond has the highest configurational entropy of all materials, as such it can pick up energies of all magnitudes from infrared (thermal) to ultraviolet (particles) and drive electrons to form electricity. Amorphous diamond is also extremely radiation hard, i.e. it will not be damaged by the bombardment of extremely high-energy solar particles. Hence, amorphous diamond solar cells will not age with time as semiconductor solar cells. Consequently, its thermal electricity efficiency will remain high with time.

Because amorphous diamond is self-doped, it does not involve thermal diffusion for chemical doping, hence, the manufacturing cost can be low. In fact, amorphous diamond can be conveniently produced as a coating on almost any substrate material (e.g. most metals). The physical vapor deposition methods, such as cathodic arc or laser ablation, can be used to coat amorphous diamond for making large solar panels. A very thin coating (e.g. 1 micron) is sufficient to absorb effectively most of the sunlight.

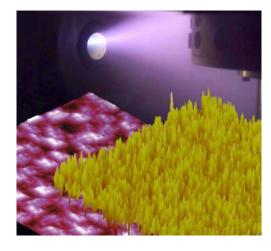


Figure 3: Amorphous diamond can be coated by spraying with carbon plasma such as that produced by cathodic arc in vacuum. The surface texture can be roughened to facilitate the electron movement along the fibrous direction.

2 COLD CATHODE FLUORESCENCE LAMP

Cold cathode fluorescence lamps (CCFL) are miniature fluorescence lamps with high brightness (e.g. 10,000 candela/m²) as shown in Table 1. They are used as back light for illuminating liquid crystal displays (LCD). LCD is the mainstream for monitors of computers and televisions. CCFL are also used extensively as the light sources for scanners, projectors, and automobile lights.

	Brightness	Backlight Brightness
Notebook	300	5000
Monitor	400	8000
Television	500	12000

Table 1: 2005 CCFL Electrode manufacturers worldwide

The principle of CCFL is illustrated in Figure 4. A sealed glass tube is coated inside with phosphor inside. For emitting white (transparent) light, three types of phosphor are mixed together, each can emit light of a distinct color with the wavelength centered at 611 nm (red), 544 nm (green) or 450 nm (blue). These emissions were triggered by ultraviolet (UV) radiation (wavelength 254-365 nm) emitted from mercury vapor that is sealed in a glass tube along with an inert gas (e.g. Ar). The UV radiation is emitted in vacuum from mercury atoms that are excited by electron bombardments. The electrons were ejected from two electrodes located at opposing ends of the lamp.

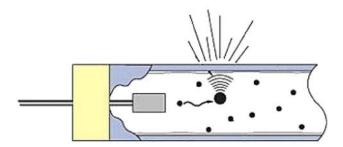


Figure 4: The perspective view of a CCFL. A example of CCFL is 430 mm in length. It is operated at 800 volts (input 12 V) with a current of 5 miliamperes. The vacuum level in the tube is about 80 torr.

The brightness of CCFL is dependent on the current of electron emission from the electrodes. In order to increase the current, the tip of the electrode is often enlarged to form a cup shape so more electrons can be ejected from the rim, as well as the inside surface of the cup instead of the needle tip with restricted size.

3 ELECTRON EMISSION BARRIER

Despite the effort to optimize the geometrical design of the CCFL, the real limiting factor is the activation energy for electrons to overcome before leaving the electrode. This energy barrier is related to work function that is sensitively dependent on the electrode material as shown in Figure 5.

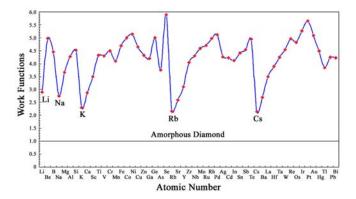


Figure 5: The periodic variation of work function that reflects the tendency of losing electrons from the material. Note that amorphous diamond has an effective work function that is lower than any material.

The emitted current is inversely related to the exponent of the work function, so a small decrease of the latter will cause a tremendous increase of the former. The amorphous diamond has an effective work function that is much lower than all other elements, hence, the electrical current is the highest under the same voltage, particularly at an elevated temperature, such as the case for the electrode of CCFL. This phenomenon of thermally excited emission is known as thermionic emission. Amorphous diamond is by far the most effective and efficient thermionic materials known.

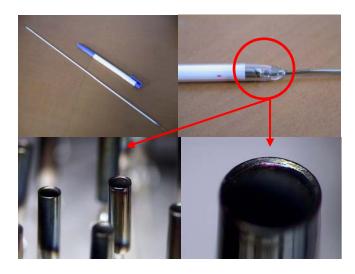


Figure 6: Amorphous diamond coated CCFL electrodes.

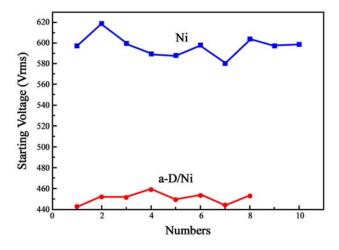


Figure 7: The significant reduction of voltage for electron emission by coating the nickel electrode with amorphous diamond.

4 CCFL EMISSIONS

A typical electrode material is made of nickel, but molybdenum has also been used. The latter materials are much more expensive, but their emitting life can be lengthened from about 20,000 hours to about 50,000 hours. However, the activation energies for both metals are very high, hence voltage must be built up to force electrons to go out. The result is that a significant voltage (about 150 V) is consumed in creating heat that consumes about 30% of the electricity power. One way to help electrons to overcome the activation energy is to coat the surface of the electrode with a lower energy barrier material, such as a cesium or lanthanum alloy. However, due to the high temperature (up to 200 °C) present at the electrode during the electron emission, the coated material will decompose or even Recently, Toshiba [1] applied boron doped diamond film of a few microns thick to molybdenum electrodes and found that the voltage drop across the electrode was reduced to less than 90 V, moreover, the power consumption was decreased by 10%. Although this breakthrough is encouraging, however, the coating must still applied to expensive molybdenum electrode. Furthermore. diamond film must be deposited by chemical vapor deposition that is low in throughput and high in cost. Consequently, more cost effective solution must be sought for commercial applications.

The electron emissions in vacuum (not CCFL) were compared between metal cup electrodes and amorphous diamond coated ones. Amorphous diamond was found to boost the electrical current density at the working voltage of CCFL by four orders of magnitude. Moreover, when the electrode was heated to 100 °C, the emitted current was increased so much that it went out of the scale as shown in Figure 8. The electrodes of CCFL is heated to about 150 °C during use, so the thermionic boost of electron emission for amorphous diamond is a great advantage.

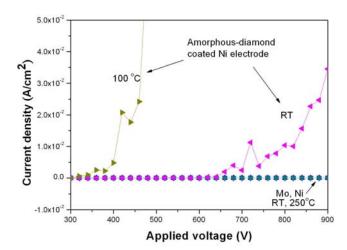


Figure 8: The dramatic increase of emitted current density by coating metal with amorphous diamond and the even larger boost of the current by modest heating. The above measurement was made by Industrial Technology Research Institute in Taiwan. The electrical current was induced by a needle anode located at 10 microns above the rim of the cup electrode. The vacuum level for the measurement was 10⁻⁵ torr.

5 CCFL LIFE

The increase of electrical current in CCFL may increase the brightness of the light. Alternatively, the operating voltage can be reduced to lengthen the service life of the lamp. In a subsequent experiment, the voltage of CCFL was measured with electrodes made of various materials, the result confirmed that amorphous diamond could decrease the starting voltage of the lamp, and hence it may increase its service life (Figure 9).

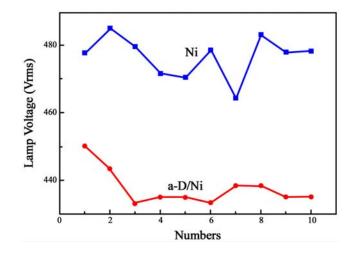


Figure 9: The voltage for CCFL operation.

Amorphous diamond can increase the service life of CCFL with another attribute, that its sputtering rate is the

lowest of all materials (Figure 10). Electron emission can sputter atoms off the electrode so the slower sputtering rate would preserve the working conditions of the electrode for a longer duration of time.

Moreover, the CCFL's life time can also be reduced by reduction the amount of mercury in the CCFL tube. Amorphous diamond would not react with mercury during CCFL operation (Figure 11). The CCFL's life time could be extended by chemical inertion.

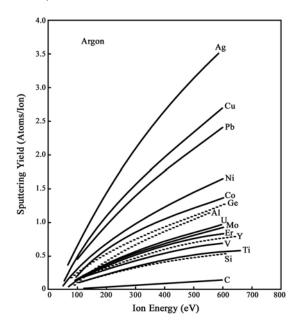


Figure 10: The sputtering yield of different material when bombarded with argon ion at different energies.

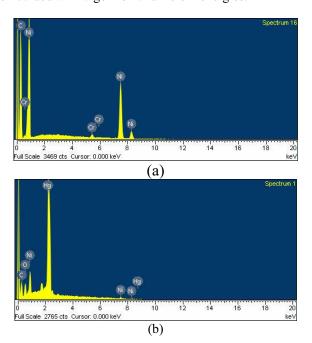


Figure 11: The EDS analysis of diamond coated (a) and Ni (b) electrode after CCFL operation for 100 hours.

6 DIAMOND ELECTRO LUMINESCENCE (DEL)

The easy flow of electricity through amorphous diamond can be applied to electro luminescence (EL) that has limited commercial application due to low luminosity and short life. By using amorphous diamond as the cathode, replacing conventional silver grease, EL is converted to DEL that may be brighter and last longer as demonstrated below.

7 AMORPHOUS DIAMOND THERMAL RADIATOR

The thermal electricity phenomenon of amorphous diamond can be used to radiate heat in air instead of electrons in vacuum. All materials can emit infrared waves upon heating due to black body radiation. However, the emissivity of metals is very low (e.g. 1%). On the other hand, non-metallic substances (e.g. ceramics) has poor thermal conductivities (e.g. 1/10 of metal). Amorphous has nearly 100% emissivity and its thermal conductivity is higher than even silver, the best thermal conductor of all Consequently, amorphous diamond can radiate heat efficiently. This ties in with its unique ability to accumulate phonons. According to Stefan-Boltzmann equation, the power of black body radiation may be calculated as $5.67 \times 10^{-8} \text{ T(K)}^4 \text{ W/m}^2$. As an example of T = 363 K (90 °C), the power radiated is about 0.1 W/cm² that is about 10% of the input power of LED. The radiated infrared wave is 2.9 x 10-3 m/T(K) = 8 μ m, according to Wien's Law. Such a high rate radiation can accelerate air convection so the heat flow is continuous. consequence, the cooling effect can be substantial.

REFERENCES

- [1] H. Yoshida, I. Yanase, N. Sakuma, T. Ono and T. Sakai: 8th International Conference on Applications of Diamond and Related Materials/1st NanoCarbon Joint Conference, Argonne National Laboratory, USA (May, 2005)
- [2] Ming-Chi Kan, Jow-Lay Huang, James C. Sung, Ding-Fwu Lii, Kue-Hsien Chen: International Conference of New Diamond Science & Technology, Melbourne, Australia (July, 2002)
- [3] T. S. Fisher: Applied Physics Letters 79, 22 (2001) 3699-3701
- [4] James C. Sung: Industrial Materials (Chinese), September (1998) 114-123
- [5] James C. Sung: Industrial Materials (Chinese), October (1998) 152-164
- [6] V. A. Solntsev and A. N. Rodionov: Solid State Electronics 45 (2001) 853-856
- [7] Chien-Min Sung, 2004, U.S. Patent No.6,806,629
- [8] Chien-Min Sung, 2005, U.S. Patent No.6,949,873
- [9] Chien-Min Sung, 2005, Taiwan Patent No.I230740
- [10] Chien-Min Sung, 2003, China Patent Application No.03130999.2