LIQUID SEMICONDUCTOR DIODE AS A THERMAL HARVESTER FOR HIGH TEMPARATURE APPLICATIONS

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Abstract: This paper describes thermal harvesting characteristics of liquid semiconductor diode. We have fabricated and characterized a MEMS-based Schottky diode using a liquid semiconductor (Selenium). Large open-circuit voltage 2.1V and short-circuit current 28μA at 350°C are also observed. By employing a direct thermal to electrical energy conversion, a 14μW is harvested at 350°C from the micro liquid semiconductor Schottky diode.

Key words: thermal harvesting, liquid semiconductor, diode

1. INTRODUCTION

The demand for energy is expanding for reliable energy, low cost, and environmental friendly. To meet this demand, energy harvesting has been explored vigorously from many resources such as solar power, wind power, fluid flow, thermal gradients, gravitation, and energy from the human body [1]. Among those, harvesting energy from thermal gradients shows significant advantage due to their silent operation, no moving part, low maintenance and high reliability. A thermal gradient can be simply found in daily life such as heaters, air conditioners, car engines etc. The great amount of heat energy is simply wasted. Thermal to electrical energy conversions by using thermoelectric and thermionic effects have been widely attempted [2]. In addition, for favorable thermoelectric properties, many researchers have been investigating new techniques employing nano-wire, super lattices, and heterostructures [3, 4].

Generally, when the temperature gradient applied between two ends of metal or semiconductor, electrons from the hotter side gain kinetic energy and flow to the colder side due to the Seebeck effect. However, there is a well-known problem, degradation effect of carriers at high temperature.

This paper presents a new thermal harvester based on liquid semiconductors. Our approach is based on the idea of separating electron hole-pairs (generated from thermal energy) by built-in potential in a PN junction. It is similar to the solar cell's principle other than using thermal energy. A liquid semiconductor material is implemented to avoid the degradation effect of carriers at high temperature. In liquid phase, liquid semiconductor naturally wets the surface of the electrode very well and provides better electrical contacts with metal electrodes comparing to the contacts in solid state semiconductors.

2. DESIGN AND MATERIAL

For the micro thermal harvesting experiment, a liquid-semiconductor-based Schottky diode is developed. As shown in Figure 1, the diode design is composed of a liquid semiconductor sandwiched between two electrodes. The liquid semiconductor is enclosed in a SU8 reservoir with 10μm height and 11.28mm in diameter (which corresponds to the area of 1cm^2). Aluminum is used as a Schottky contact electrode on the bottom substrate, and nickel is used as an ohmic contact electrode on the cover substrate. A special conductive epoxy for high temperature applications is used for the interconnection between the top and bottom electrodes.

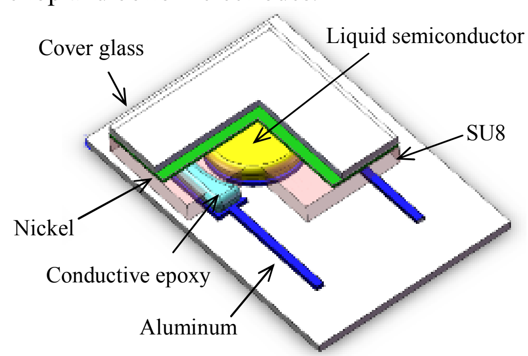

Fig. 1: 3D view of the micromachined liquid semiconductor diode as a thermal harvester.

Selenium has semiconducting properties in both solid (amorphous) and liquid state [5]. The chemical bond model of amorphous selenium is categorized to be lone pair semiconductors (twofold coordination) because the electron configuration is [Ar]$3d^{10}4S^{2}4p^{4}$, which implies that the properties of Se are primary influenced by two non-bonding of P orbital of group 16 chalcogen, which exhibited in covalent interaction boning [6]. Se atom tends to bond in lone pair semiconductor in either helical chain (trigonal phase) formation or Se_8 ring (monoclinic phase) formation. Once Se is reach a melting temperature (T_m = 221°C), structure of the liquid phase Se is mostly change into a planer chain polymer with the average of 10^4~10^6 atoms per chain near T_m, and a small fraction of Se_8 ring [7]. In liquid semiconductor, electrical conductivity increases when temperature and pressure increases [8].

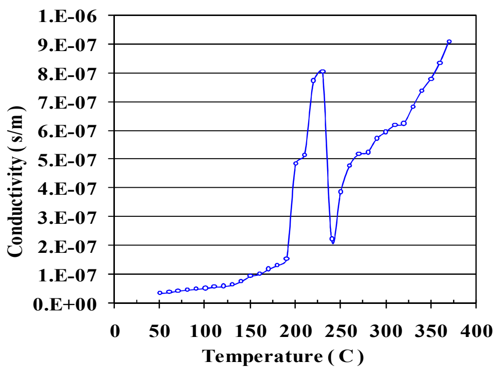

Fig. 2: Electrical conductivity vs. temperature on pure selenium.

As shown in Figure 2 from our preliminary works, we have confirm that the conductivity of pure selenium increases significantly (approximately 400%) at around 230°C (melting point of Se), which is due to the deformation of composite selenium ring from both chain scission, and ring dissociation. The nature of selenium is P–type semiconductor and has large energy gap (1.85 eV) and high electron affinity (5.9eV) which results in a large potential barrier across a depletion region and large diffusion length for ideal Schottky junction of thermal harvester. In case of an ideal schottky diode which employing selenium as a P-type semiconductor, the Schottky barrier height ϕ_{BP} is given by:

$$\phi_{BP} = \frac{E_g}{q} + \chi_s - \phi_m$$

where E_g is the energy gap, q is electron charge, χ_s is electron affinity, and ϕ_m is the work function. A metal with low work function is employed in contact to the liquid semiconductor material for ensuring ideal Schottky barrier height.

Since the electron is charge particle, it produces the space charge region between a cathode and an anode. This space charge region can be reduced by introducing positive ion between the two electrodes, using electromagnetic to conduct electron between the gaps or reducing the gap distance [9]. Similarly, we have reduced the gap distance and neutralized the space charge by utilizing a p-type semiconductor material. Additionally, for higher efficiency, a cathode with a smaller work function (nickel) than anode (aluminum) is employed. The maximum possible of Carnot efficiency can be express as

$$\boldsymbol{\eta_c = 1-(\varphi_c/\varphi_a)}, \qquad (2)$$

where $\boldsymbol{\varphi_c}$ and $\boldsymbol{\varphi_a}$ are the work function of cathode and anode respectively.

3. FABRICATION AND TESTING

The brief fabrication steps are as illustrated in Figure 3. First, a bottom electrode (0.3µm of aluminum layer) is deposited on a glass substrate by sputtering and patterned with a standard photolithography process. Then, a 10µm-thick SU-8 reservoir is formed to contain a liquid semiconductor. The top electrode (0.2µm of nickel layer) is evaporated on another glass substrate (as a cover substrate) and patterned. After selenium is confined in the reservoir, the device is enclosed by the cover substrate by using thermocompression bonding technique. A conductive epoxy with high temperature stability is applied for the electrical interconnection between the top and bottom electrodes.

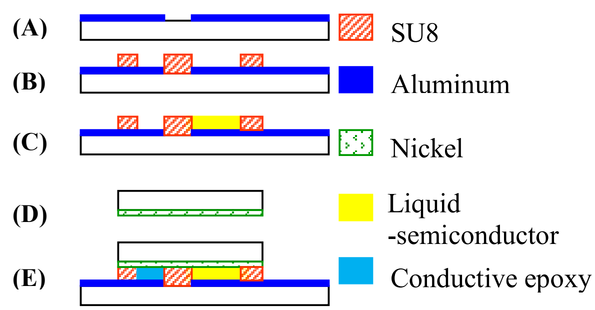

Fig. 3: Fabrication process.

The fabricated device on a test stage is shown in Figure 4. The liquid semiconductor is confined within the circle in the middle of the device. The experimental set up consists of a HP Semiconductor Parameter Analyzer (4145B), micro manipulators, a hotplate and low level signal probes with precision probe manipulators. A data acquisition connection (HP-GPIB) to a PC and software (Labview 8.2) are used to analyze the data from the Semiconductor Parameter Analyzer. I-V characteristics data of the device are precisely analyzed from this setup.

To simulate a heat source, we have used a hot plate with accurate temperature controllability. The temperature was varied between 50°C and 350°C and the I-V characteristics data at every 50°C were measured from the device.

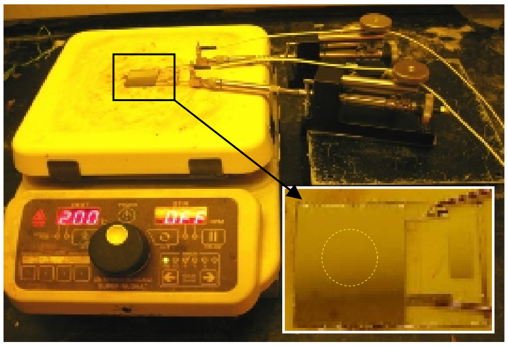

Fig. 4: Picture of the fabricated thermal harvester and the experimental set up.

4. RESULTS AND DISCUSSION

From the I-V characteristics at the various temperature points between 50°C and 350°C, we have found rectifying curves as shown in Figures 5 and 6. The turn on voltages in the forward bias region are between 0.5V and 1.2V (Figure5). The rectification characteristic improves when temperature increases from 50 °C to 200 °C. This is because of the reduction of conduction band by the raised hole mobility from the temperature increase. The reverse saturated current is found to be 1.1nA at 50°C, and 55nA at 100°C, respectively. The breakdown voltage at high temperature reduces because the reverse bias current density is proportional to the temperature increase (Figure 5). A small breakdown voltage between 0.8V to 2V is found in the reverse bias region.

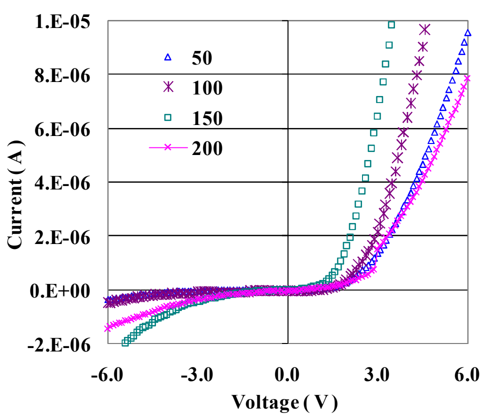

Fig. 5: I-V curve of selenium liquid semiconductor at different temperature from 50 to 200 °C.

Figure 6 illustrates the I-V characteristics of the molten selenium between 250-350°C. The turn on voltages increase as the temperature increase from 200°C to 350°C due to the diffusion at the depletion region is efficiently formed and/or the reduction of contact resistance when temperature increases. The reverse bias current continuously increases without being saturated and the dark currents (negative current without external bias) are observed at the temperature at temperature higher than 200°C. Some experimental data show that the I-V characteristics move upward (quadrants 2) or downward (quadrants 4) due to the reverse sign of Seebeck coefficient upon melting point. The dark current area of liquid selenium between 200°C and 350°C is magnified and shown clearly in Figure 7. As temperature reaches 250°C, selenium turned into a liquid phase. The open-circuit voltage (V_{oc}) increases instantaneously from 0.6V at 200°C to 3.5V at 250°C, and keeps increasing as the temperature increases. This open-circuit voltage is significantly higher than the thermoelectric power of a bulk selenium (Seebeck coefficient of pure selenium is about 1~1.3 mV/°C at 300°C [10]).

On the other hand, the short-circuit current (I_{sc}) stays increasing. This is because the conductivity of the liquid semiconductor (selenium) increases. This device shows a maximum short-circuits current of 28.9µA at 350°C

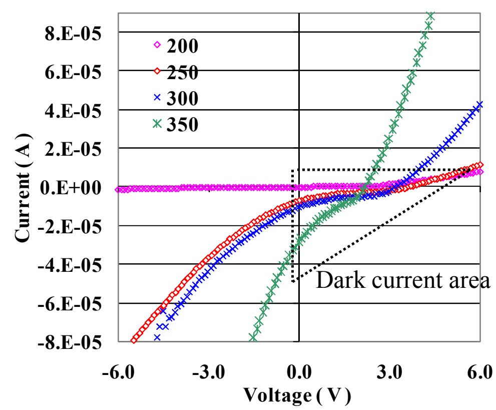

Fig. 6: I-V curve of selenium liquid semiconductor at different temperature from 200 to 350 °C.

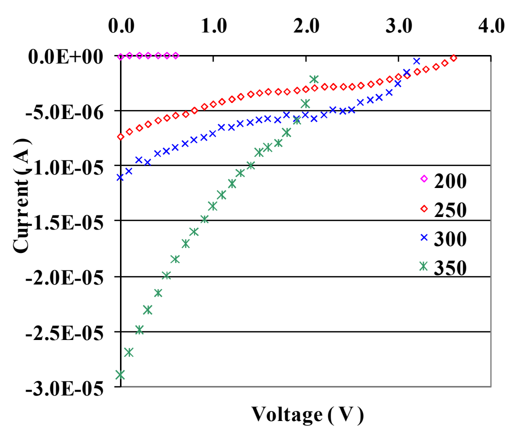

Fig. 7: Magnified graph of the dark current area.

Figure 8 show the output power against bias voltage. The maximum power of 14µW was obtained at 1.2V from the hotplate's temperature of 350°C. Figure 9 illustrates the power harvesting characteristics while temperature changes. The output power increases quickly at 200°C (0.56µW), and then stay saturated at around ten micro watt range. The maximum output power from prototype is 14µW at 350°C.

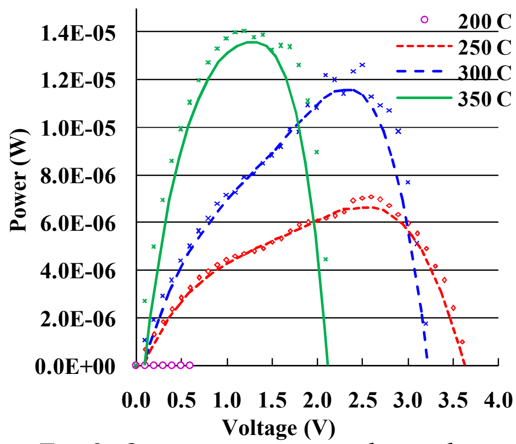

Fig. 8: Output power against bias voltage.

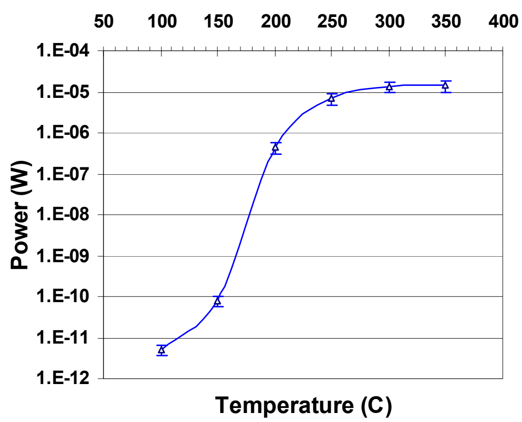

Fig. 9: Output power against temperature from 50 to 350 °C.

We have found very interesting results that the liquid semiconductor (Se) can convert heat energy into electrical energy. We believe that there are still many aspects to improve the output power. For instant, changing the electrode material with higher/lower work function and increasing the active area would affect the performance for instance build-in voltage and barrier height. Moreover, adding the impurity in the liquid semiconductor would improve the performance due to the trap energy level on the mid band gap from Shockley-Read-Hall (SRH) recombination model. We expect that these modifications would increase the higher harvesting power than the one from the prototype. Further performance enhancement is now in progress to improve the output power of the micro machined thermal harvester.

5. CONCLUSION

We have successfully shown the feasibility of a micro liquid semiconductor diode as a thermal harvester at high temperature. A prototype was developed and demonstrated to harvest 14µW at 350°C. Also, large open-circuit voltage (3.5V) and short-circuit current (28.9µA) were observed which can be used to supply more power to the load. Future work is required for deep understanding the physical mechanism of the current injection of this liquid semiconductor diode structure. This technology has a big potential for various high temperature applications.

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