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WETTABILITY OF DIAMOND BY LIQUID PURE TIN

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Abstract—The wettability of (100), (110) and (111) planes of diamond by liquid tin was measured using the sessile drop method. The atmosphere was a purified argon–10% hydrogen mixture and the temperature was between 773 K and 1773 K. The results are reproducible and clearly show that the wettability of diamond changes unusually with temperature. The changes reflect the changes in the surface condition of the diamond: the desorption of hydrogen, the reconstruction and the graphitization. Accordingly, it is concluded that the wettability measurement can also be used as a surface analyzer which also can be used at a high temperature in an ambient atmosphere. © *1998 Acta Metallurgica Inc.*

1. INTRODUCTION

Diamond can be used as a semiconductor for high temperature devices and a heat sink as well as a tool material because of its superior physical properties such as high hardness, high thermal conductivity, low thermal expansion coefficient and electronic properties. On the diamond surface, gas species such as hydrogen, water and oxygen are adsorbed at a low temperature and desorbed at a high temperature, and then at a higher temperature the surface easily changes into graphite. Accordingly, the wettability of diamond is expected to depend on the temperature significantly.

The wettability of many solid–liquid systems has been measured because it often plays an important role in material processing such as the fabrication of composites, the production of clean steel, welding, joining and casting. It is well known that the wettability is significantly affected by the surface condition of the solid. This fact implies that some information on the surface condition of the solid is available from wettability measurements.

In this study, in order to demonstrate the potential of the wettability measurement for use as a surface analyzer, the wettability of (100), (110) and (111) planes of diamond by liquid tin was measured. Clear evidence of any change in the condition of the diamond surface is obtained by measuring the wettability.

2. EXPERIMENTAL METHOD

The sessile drop method was used to measure the wettability of diamond. Figure 1 shows a schematic diagram of the furnace [1]. In this study, an infrared furnace was used as it allows the sample to be heated very quickly. Because both the sample and the thermocouple (Pt–6Rh/Pt–30Rh) were set in the focus area of the infrared lamp, as shown in Fig. 1, the difference in temperature of the sample and the thermocouple was within 10 K. In addition, the temperature was calibrated using the melting points of four kinds of pure metal (Sn, Pb, Ag and Cu).

Tin was selected as a liquid sample because the chemical affinity with diamond is low, the vapor pressure and melting point are also low. The tin used was 99.9% pure and 200–400 mg tin was used for each experiment. For the solid sample, Ib type synthetic diamonds [2] were used with a surface area of 3 mm x 3 mm. The diamond was carefully polished and annealed at 1573 K for one hour to adsorb hydrogen onto the dangling bonds of the diamond surface. As a reference material, cleaved (1000) graphite was also used.

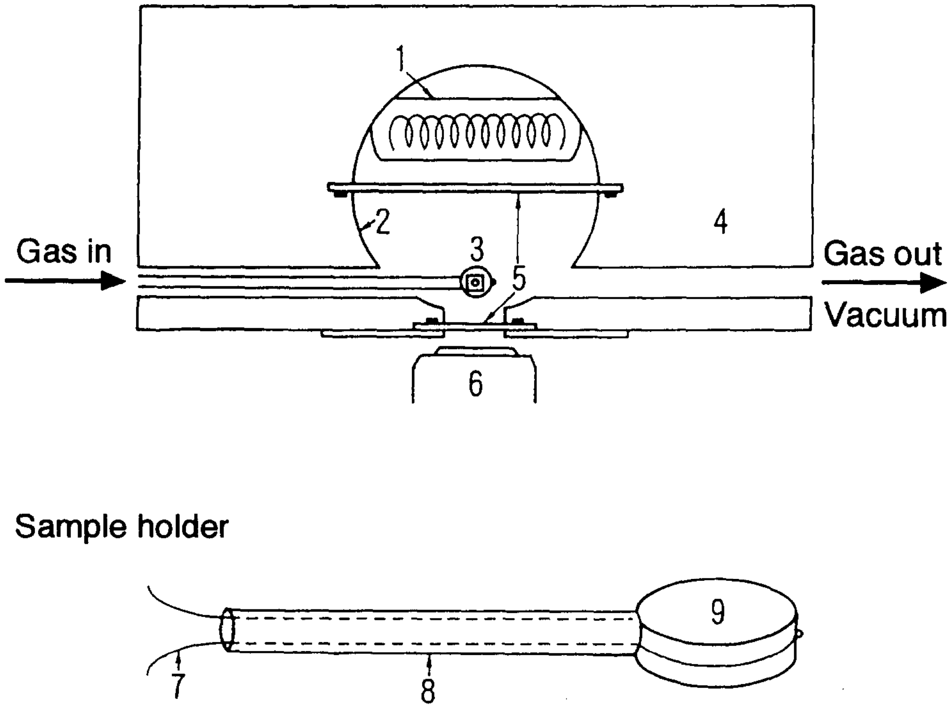
The atmospheric gas was an argon–10% hydrogen mixture. The gas was purified by being passed through a silica gel, a magnesium perchlorate, platinum asbestos and a dry ice–methanol mixture cold trap in order to remove oxygen and water. After the chamber had been evacuated for one hour, the purified gas was introduced. The gas was forced to flow slowly for 3 h, and then the measurement of the contact angle was started, maintaining the gas flow.

The experimental temperature was raised by 50 K for 2 min. The sessile drop was magnified 25–400 times by a microscope and photographed with a 35 mm camera. The contact angle was directly measured on projections of the negative film (magnification 20x). In addition, in order to analyze the surface condition of diamond, the XPS analyses have been performed under vacuum after quenching some samples.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Change in contact angle of tin on diamond with temperature

Figure 2 shows the change in the contact angle of liquid tin on the diamond (100) plane with increas-



1. Infrared luminant
2. Gold mirror
3. Sample holder
4. Water jacket
5. Quartz glass
6. Optical microscope
7. Thermocouple
8. Alumina tube
9. Alumina holder

Fig. 1. Infrared image furnace (seen from the top) and sample stage.

ing temperature. It can be seen in Fig. 2 that the contact angle changes unusually with temperature, but that the results are reproducible. These results indicate a change in surface condition of diamond with temperature. The contact angle suddenly decreases from 160° to 100° at about 1050 K. The contact angle increases to 120° at 1250 K and further increases to about 150° at 1750 K.

Figure 3 shows a schematic illustration of the expected surface change of diamond with temperature. The surface energy of the diamond with dangling bonds terminated by hydrogen should be low, and the surface energy is high at the medium temperature because the dangling bonds are free from hydrogen [3]. At a higher temperature, the surface energy decreases again because the surface becomes graphitized.

Table 1 summarizes the desorption temperature of hydrogen from the diamond surface under an ultra high vacuum [4–7]. These data indicate that the dangling bonds of all diamond surfaces are terminated by hydrogen at a temperature lower than 1073 K and that at a temperature higher than 1273 K none of the dangling bonds are terminated in any plane. Unfortunately, the dependence of surface orientation on the graphitization temperature has not yet been reported.

It is easily found that the temperature where the contact angle suddenly decreases in Fig. 2 is very close to the desorption temperature. It is considered that the increase in contact angle at 1750 K is attributed to the graphitization of the diamond surface because diamond is a metastable state of graphite and changes to graphite at a high temperature [8]. Figure 4 shows XPS spectra of the diamond (100) plane, the results of (110) and (111) planes will be discussed later. Although the peak is still located between the peaks of graphite (284.9 eV) and diamond (289.3 eV), it is close to that of graphite. Therefore, it can be concluded that the graphitization had progressed considerably at 1750 K. On the other hand, it is considered that the

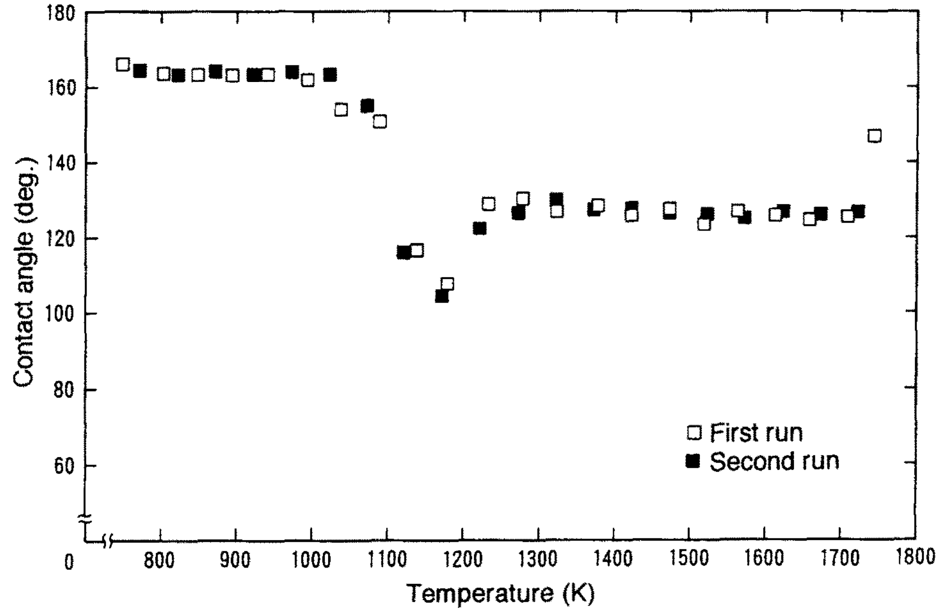


Fig. 2. Variation of contact angle between liquid tin and diamond (100) with temperature in argon–10% hydrogen atmospheric gas.

increase in contact angle at around 1250 K is caused by the reconstruction of the diamond surface, because the diamond surface after the hydrogen desorption has a high surface energy. In fact, the reconstruction of diamond surface has been confirmed with LEED analyses by Pate *et al.* [4, 5].

Figure 5 shows the results for diamond (111) plane. A similar tendency was also observed in this plane. The contact angle decreased at about 1000 K and increased at about 1250 K. In addition, the increase in contact angle due to the graphitization was also observed in this plane around 1750 K. Although the contact angle started to decrease at a temperature lower than the desorption temperature of hydrogen (1273 K) shown in Table 1, it does not contradict with the above consideration because the desorption usually starts at a temperature lower than the main desorption temperature [4].

Naidich has reported the contact angle of tin on diamond between 1173 K and 1473 K, as shown in Table 2 [9], though the surface orientation is unknown. These values are close to the contact angle after the sudden increase at around 1250 K in this study.

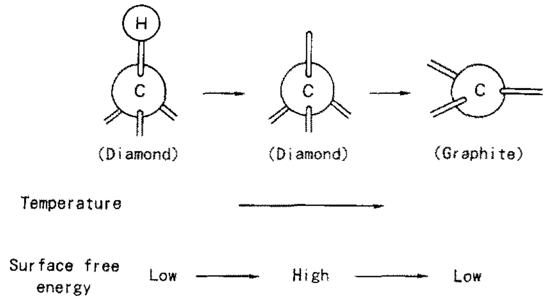


Fig. 3. Change in surface condition of diamond with temperature.

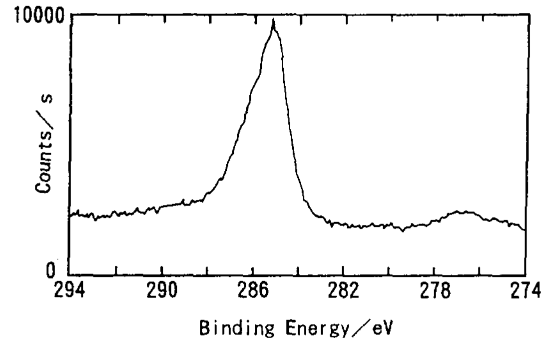
3.2. *Hysteresis of contact angle with temperature*

The change in contact angle values for the (110) plane is given in Fig. 6 and photographs showing the characteristic changes in the contact angle are presented in Fig. 7. On this plane, the change in contact angle indicates the change in the surface condition: the desorption of hydrogen, the reconstruction and the graphitization of the diamond surface too. However, on this plane, the contact angle also displayed a sudden decrease at around 1550 K. This decrease probably corresponds to the release of the reconstruction of the diamond surface. It is considered that at such a high temperature as 1550 K, the release of the reconstruction can occur due to the entropy term.

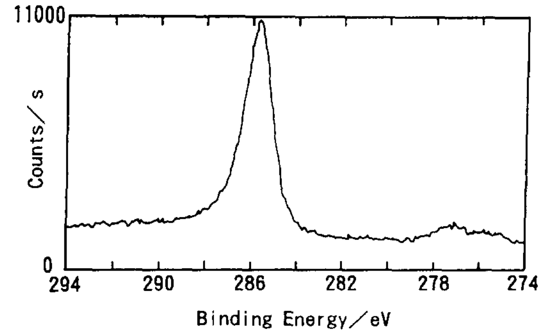
In order to investigate the hysteresis of the change in contact angle, the contact angles were also observed with decreasing temperature. As can be seen in Fig. 8, the change in contact angle at around 1550 K is found to be reversible. This result is consistent with the hypothesis that the change in contact angle at this temperature is caused by the release of the reconstruction of the diamond surface.

Table 1. Desorption temperature of hydrogen from diamond surface in UHV (10^{-8} Pa) [4–7]

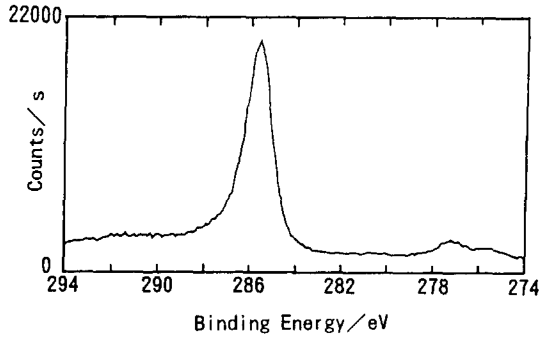
(*hkl*)	Temperature of desorption (K)
(100)	1073
(110)	1173, 1223
(111)	1273



(a) diamond(100)



(b) diamond(110)



(c) diamond(111)

Fig. 4. XPS spectra of diamond surface heated at 1723 K.

The unusual change in the contact angle between 1250 K and 1000 K is not observed while the temperature is decreasing. This is probably because the hydrogen is directly adsorbed on the reconstructed diamond surface without passing through the non-reconstructed state. In the experimental atmosphere of this study, tin is not oxidized in term of thermodynamics, because the partial pressure of H_2O is reduced. However, because of the kinetic reason, the sample at the beginning of the experiments may still be covered with an oxide film. The hysteresis in the contact angle below 1000 K is probably caused by this reason.

Figure 9 shows the change in contact angle of graphite with both increasing and decreasing temperature. The contact angle does not change very much because graphite does not have dangling-bonds on the surface and thus the surface condition does not undergo much change. Accordingly, it can be concluded that when the surface condition does not change greatly, the contact angle does not depend on whether the temperature is increasing or decreasing.

Table 2. Reported values of contact angle of liquid tin on diamond [9]

Temperature (K)	Contact angle (°)
1173	125
1273	125
1373	125
1473	124

3.3. Wettability and surface analysis

The wettability is determined by only several atomic layers from the surface of the solid. In this sense, the wettability measurement is one of the best methods of obtaining information about the surface. In the diamond/tin system, changes in the surface condition such as the graphitization and the desorption of hydrogen are reflected in the wettability very clearly.

When the wettability measurement is used as a surface analyzer, the liquid metal has to be carefully chosen and the following points should be taken into account.

(1) The chemical affinity between the solid being analyzed and the liquid metal should be low.

(2) The vapor pressure of the liquid metal should be low.

(3) The melting point of the liquid metal should be low.

(4) The liquid metal should not easily be oxidized.

Thus, when you find a metal meeting these conditions, you can easily discover changes in the surface condition of the solid from the wettability measurement. In addition, using a reference material such as graphite for diamond, it is also possible to estimate indirectly how the surface condition changes. As shown in Fig. 9, the contact angle of tin on graphite was 155° at 1750 K, and found to be close to the value obtained for diamond. It can be concluded from these values that the diamond changed to graphite at 1750 K. Thus, the wettability measurement can be used as a cheap surface analyzer. In addition, this method can be used at a high temperature and an ambient atmosphere at which we really want to know the surface condition.

4. CONCLUSION

The wettability of (100), (110) and (111) planes of diamond by liquid tin was measured between 773 K and 1773 K in a purified argon–10% hydrogen mixture. As a result, the following points have become clear:

(1) The wettability of diamond changes unusually with temperature and the results are reproducible.

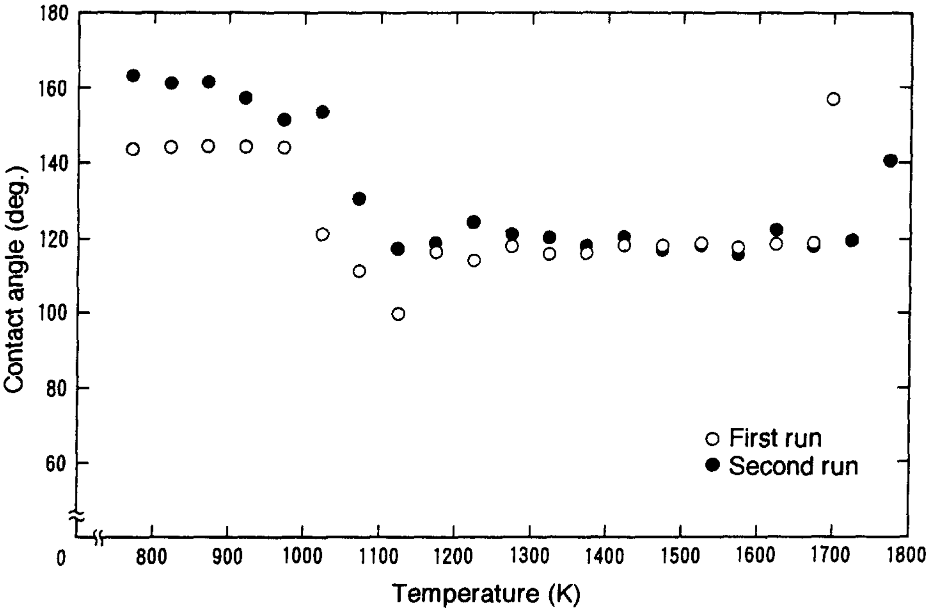


Fig. 5. Variation of contact angle between liquid tin and diamond (111) with temperature in argon–10% hydrogen atmospheric gas.

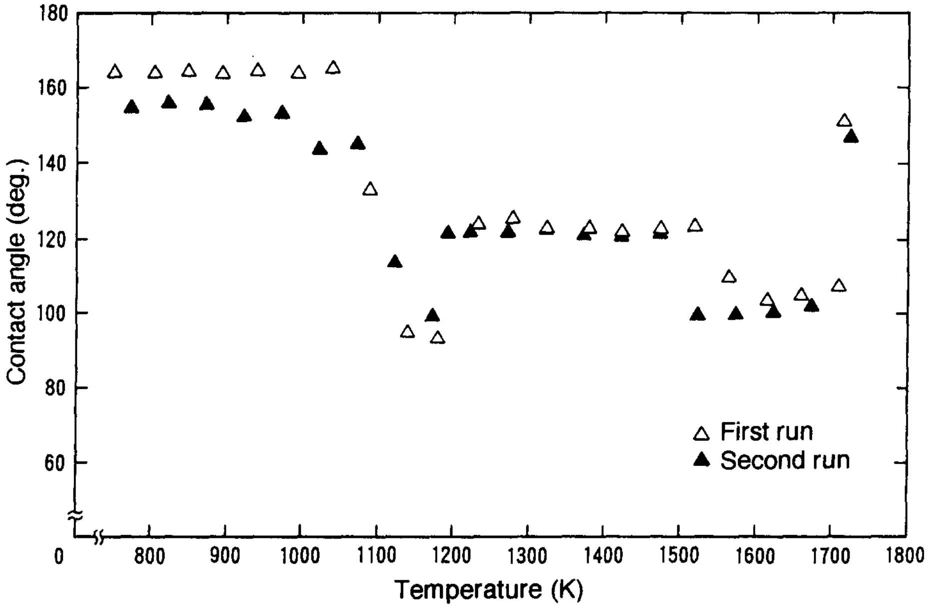


Fig. 6. Variation of contact angle between liquid tin and diamond (110) with temperature in argon–10% hydrogen atmospheric gas.

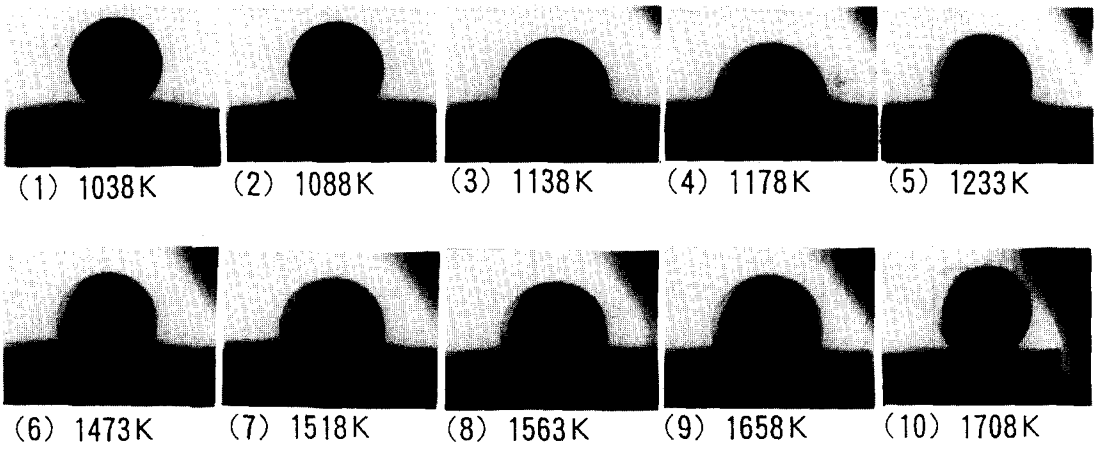


Fig. 7. Change in shape of liquid tin on diamond (110) with temperature in argon–10% hydrogen atmospheric gas.

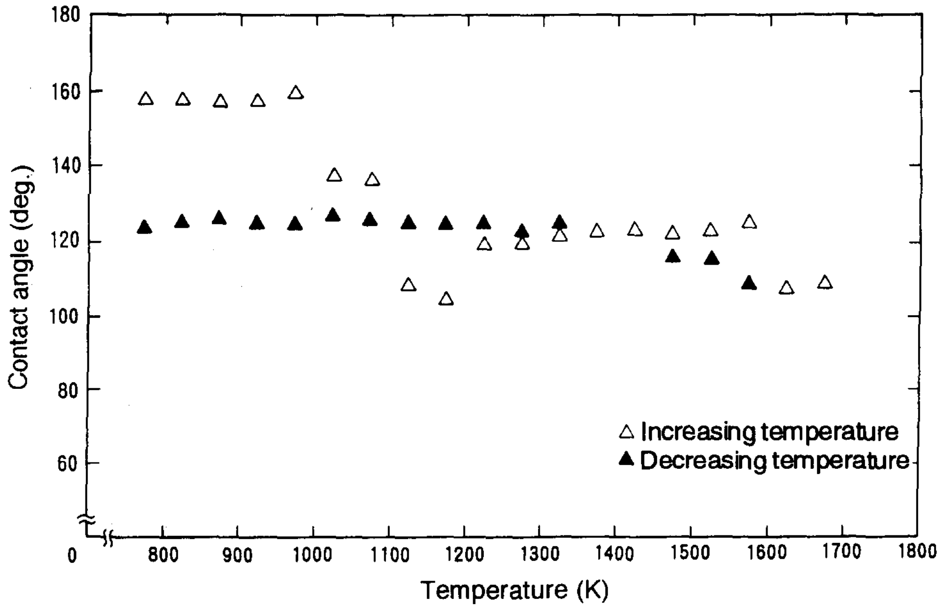


Fig. 8. Effect of temperature hysteresis on contact angle between liquid tin and diamond (110).

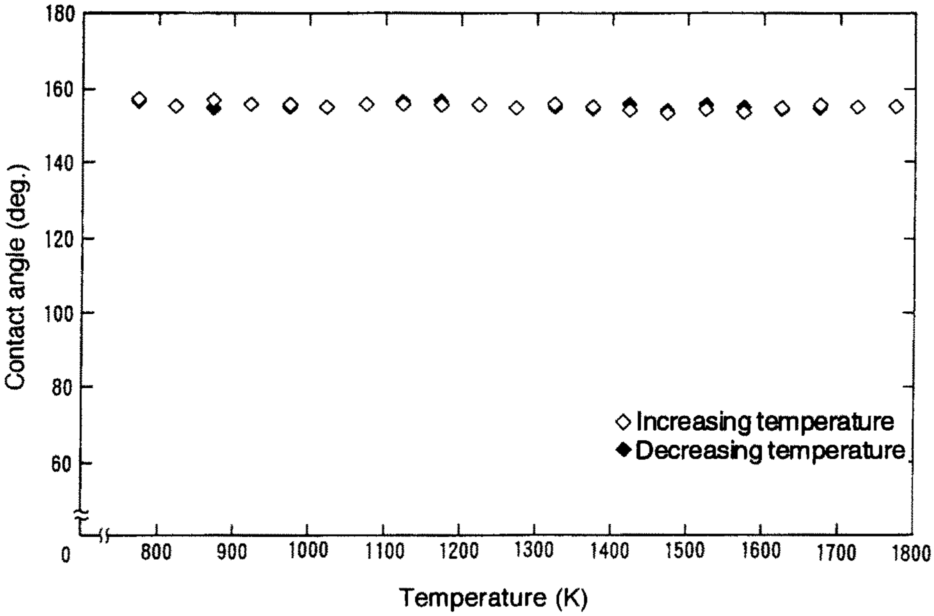


Fig. 9. Effect of temperature hysteresis on contact angle between liquid tin and graphite.

The changes are caused by the changes in the surface condition of the diamond: the desorption of hydrogen, the reconstruction of the surface and the graphitization at a high temperature.

(2) The changes in contact angle reflect the changes in the surface condition of diamond. Accordingly, it is possible to use the wettability measurement as a cheep surface analyzer which can be used at a high temperature and an ambient atmosphere.

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