USING HIGH TEMPERATURE ELECTRICAL RESISTIVITY MEASUREMENTS TO DETERMINE THE QUALITY OF DIAMOND FILMS

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ABSTRACT

The electrical resistivity of undoped diamond films has been measured between room temperature and 1200 C. The films were grown by either microwave plasma CVD or combustion flame at various different companies. It was found that the room temperature resistivities were all around 10^{15}-10^{16} Ω-cm, which has been shown to be the apparatus-limited value (higher resistivities cannot be measured). Hence, these resistivity measurements cannot indicate which of the films, which all have very similar Raman spectra, are of the best quality. Also, sample treatment (such as as-fabricated, heat treated, cleaned, etc.) will effect the room temperature electrical resistivity because of different surface conditions. On the other hand high temperature measurements up to 1200 C clearly do show differences for samples that had the same electrical resistivity at room temperature. The high temperature resistivities varied from about one order of magnitude lower than that for natural type IIa diamond to about two orders of magnitude greater over the whole temperature range with activation energies between 1.5 and 1.6 eV. These high temperature measurements are thus very helpful in determining the quality of undoped diamond films.

INTRODUCTION

The quality of diamond films synthesized by CVD, arcjet and combustion flame has improved greatly over the past few years. This improved quality has been observed optically (very clear diamond films) and in the Raman spectra that are now nearly the same or even identical to that for natural diamond (without the additional peaks indicative of nondiamond phases such as graphite, amorphous carbon etc.). Also, the thermal conductivity and electrical resistivity of diamond films have approached, equaled and in some cases exceeded that for the best natural type IIa diamonds [1,2]. However, there is no quick and accurate method of determining the quality of a diamond film. The Raman spectrum is sensitive to sp^2 bonded carbon (non-diamond carbon) but not other defects

while the room temperature thermal conductivity, which is not easy to measure accurately, is determined by impurity, grain boundary, and phonon-phonon scattering. So a high purity small grain size film could have a very low thermal conductivity. The electrical conductivity is very sensitive to all impurities and defects involved in the conduction process but at room temperature the lowest conductivities (of the best samples) exceed the limits of the measuring apparatus [3] so cannot be determined. In addition, room temperature resistivity measurements depend on the condition of the surface of the film [2,3] making interpretation of the data very difficult. However, the conductivity of diamond increases with increasing temperature making measurements easier at higher temperatures. As a result, high temperature (up to 1200 C) electrical conductivity data can be used as one of the main determinants of the quality of diamond films as the results presented in this paper will show.

EXPERIMENTAL DETAILS

The experimental approach utilized for resistivity measurements has been described elsewhere [3]. Briefly, the resistivity is measured perpendicularly through the sample, which is placed in an alumina holder. The top and bottom electrodes are iridium foils, with the sample resting on one foil and the second foil pressed against the sample by means of a niobium rod (with a small weight placed on it). Iridium was used since it does not form a carbide with the diamond at the temperatures used in the measurements. This type of electrode configuration does result in ohmic behavior in the range of voltages used (+100 V to - 100 V) [3,4]. A Keithley 617 electrometer (high output impedance) was used for the measurements. Originally a guard ring was used on the larger samples but it was found that identical results were obtained without a guard ring on the heating curve up to 1200 C as long as the data were taken within a period of several hours. This result made it possible to dispence with the guard ring, which is an advantage since it is very difficult to use on small and irregularly shaped samples. The vacuum level in the test station was 10^{-5}-10^{-6} Torr.

The diamond films were supplied by several different companies. Crystallume supplied two samples: the first (6 μm thick on Si) was grown a few years ago using their then standard process while the second one was a free standing, clear, colorless film 300 μm thick grown recently by microwave plasma CVD using their high purity technique. The Norton sample was a free standing greyish film 1.1 mm thick grown by their arcjet process. The Lockheed sample was a clear free standing film 80 μm thick grown using their combustion flame technique. Finally, the Raytheon sample was a clear free standing film 660 μm thick grown using their microwave plasma CVD technique. All the samples except the first Crystallume sample were polished (at least on one side) and cleaned before measurement. Raman spectra were also taken after growth.

EXPERIMENTAL RESULTS AND DISCUSSION

The electrical conductivity versus inverse temperature between room temperature and 1000-1200 C for the two Crystallume, the Norton and the Raytheon diamond films are shown in figure 1 and for the Lockheed film in figure 2. The conductivity of natural type IIa diamond is shown for comparison. The conductivity of this natural diamond is approximately constant in the 10^{-15}-$10^{-16}\Omega^{-1}cm^{-1}$ range between room temperature and 200 C. This is the "apparatus-limited" value which is the lowest conductivity the apparatus will measure and represents the leakage currents around the sample through the holder [3]. All samples, except the first Crystallume sample, also show this "apparatus-limited" value with the second Crystallume, the Lockheed, and the Raytheon samples having this value up to the 200-300 C range while the Norton sample has it up to about 130 C. These four samples thus all have resistivities that would be expected to be greater than $10^{16}\Omega$-cm at room temperature. This is a great improvement over samples grown only a few years ago (as a comparison with the first Crystallume sample clearly shows). The fact that three of the films have lower conductivities than that for natural type IIa diamond over the whole temperature range, indicates that these polycrystalline films have less defects (that are involved in the conduction process) and are thus purer than a good quality single crystal diamond. The Norton sample was not made with purity in mind but was made for thickness. The slightly higher conductivity for this sample in the 150-1000 C range shows that eventhough four of the samples all have the same "apparatus-limited" room temperature conductivity, the high temperature conductivities can differ by 2 to 3 orders of magnitude. Similarly, the first Crystallume sample has a room temperature conductivity of about $10^{-15}\Omega^{-1}cm^{-1}$, which is right at the limit of the apparatus, but has a very noticeably higher conductivity at higher temperatures. These results thus clearly indicate that the room temperature resistivity measurement by itself is not sufficient to determine the quality of a diamond film. Also, the Raman spectra of all the samples were all nearly equal to if not identical to that for natural diamond (with no additional peaks). Hence, the Raman spectra alone cannot indicate the comparative quality of the films as high temperature resistivity data can. The activation energies of the four low conductivity films and of the natural IIa diamond are all in the 1.50-1.60 eV range. This energy is believed to be associated with the isolated substitutional nitrogen [5].

The cooling curves for the five samples are not shown in figures 1 and 2 but cooling curves are show for the Norton sample in figure 3. The cooling curves for the other samples were very similar and were omitted for clarity. The higher conductivity on the cooling curve is due to surface leakage paths that result from surface reconstruction (above about 900 C) and surface graphitization. This non-diamond carbon surface contaminant can be removed in concentrated acids, restoring the original low conductivities. Re-heating the samples then resulted in data falling exactly on the original curves. Other contaminants as Well as non-diamond carbon will also result in higher conductivities. This can clearly be seen in figure 3 where the conductivity for the film in the as-received condition (not cleaned after polishing and cutting) has a high conductivity (about 10"1 $^{1}\Omega^{-1}cm^{-1}$) while after an acid clean the conductivity drops to the "apparatus-limited" value. Based on this result it is suspected that numerous room temperature electrical resistivity results, reported in the literature, probably were measured on "dirty"

samples so were not indicative of the true resistivity of the samples. As a point of interest a few years ago the samples we measured only had room temperature conductivities in the 10^{-14} to $10^{-10}\Omega^{-1}cm^{-1}$ range [3] and the conductivities only approached that of natural diamond at the highest temperatures. The quality of the current diamond films is thus significantly better than those synthesized only a few years ago.

Hydrogen adsorbed to the diamond film surface, as a result of the synthesis in a hydrogen-hydrocarbon atmosphere, also results in a higher conductivity with a different temperature behaviour, if it is not removed. An as-fabricated microwave plasma CVD diamond film grown at North Carolina State University had a conductivity that was approximately constant at $10^{-10}\Omega^{-1}cm^{-1}$ between room temperature and 300 C and then followed the conductivity for the natural diamond up to 1000 C. On the cooling curve the conductivity came back to $10^{-15}\Omega^{-1}cm^{-1}$ at room temperature [2]. The lower conductivity is thus the real conductivity of the film. The adsorbed hydrogen, which had probably come off by 300 C, has a pronounced effect and underestimates the resistivity of the diamond film if only room temperature values are measured.

The effect of surface finish on the measured conductivity was found to have only a slight effect as is shown in figure 2 for the Lockheed sample. This combustion flame grown film had a polished side (where the substrate was removed) and a rough side (growth side). The conductivity of the sample with the polished side up is as low as that found for the Crystallume and Raytheon samples (see figure 1), but is about one order of magnitude higher than that found with the rough side up. This lower conductivity is believed to be due to the top iridium electrode foil, which is pressed against the sample, only making contact with the diamond crystallite peaks and top facets, so not making uniform contact over the full area of the foil. In the case of the polished surface uniform contact is very likely made over the whole foil area and the correct conductivity measured. This was confirmed by putting a graphite cement contact, of the same size as the top Ir foil, on the polished side and then performing the measurement as usual. The conductivity was found to be the same as before as shown in figure 2. Care should thus be taken when measuring rough diamond surfaces. The advantage of using press contacts, rather than bonded contacts, is that the diamond film is in no way affected so can be used for other tests or measurements.

SUMMARY

The electrical conductivity of five diamond films has been measured between room temperature and 1000-1200 C. Eventhough the room temperature conductivities were all very similar and equal to the "apparatus-limited" value of 10^{-15} to $10^{-16}\Omega^{-1}cm^{-1}$, the highe temperature conductivities differed by up to several orders of magnitude. The Raman spectra of the films were all very similar. These results thus indicate that high temperature electrical conductivities (determined by the impurities and defects involved in the conduction process) are very helpful in determining the purity and relative quality of undoped diamond films. It has also been shown that the room temperature electrical

conductivity of a diamond film with a "dirty" surface (contaminants, non-carbon diamond, adsorbed hydrogen etc.) can be up to six orders of magnitude higher than that for a film with a cleaned surface.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. K.V. Ravi from Lockheed, Thomas Hartnett from Raytheon, Grant Lu from Norton, and Crystallume for supplying the diamond films.and the information regarding the films.We would also like to thank Dr. K.V. Ravi for the many helpful discussions. The work described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration.

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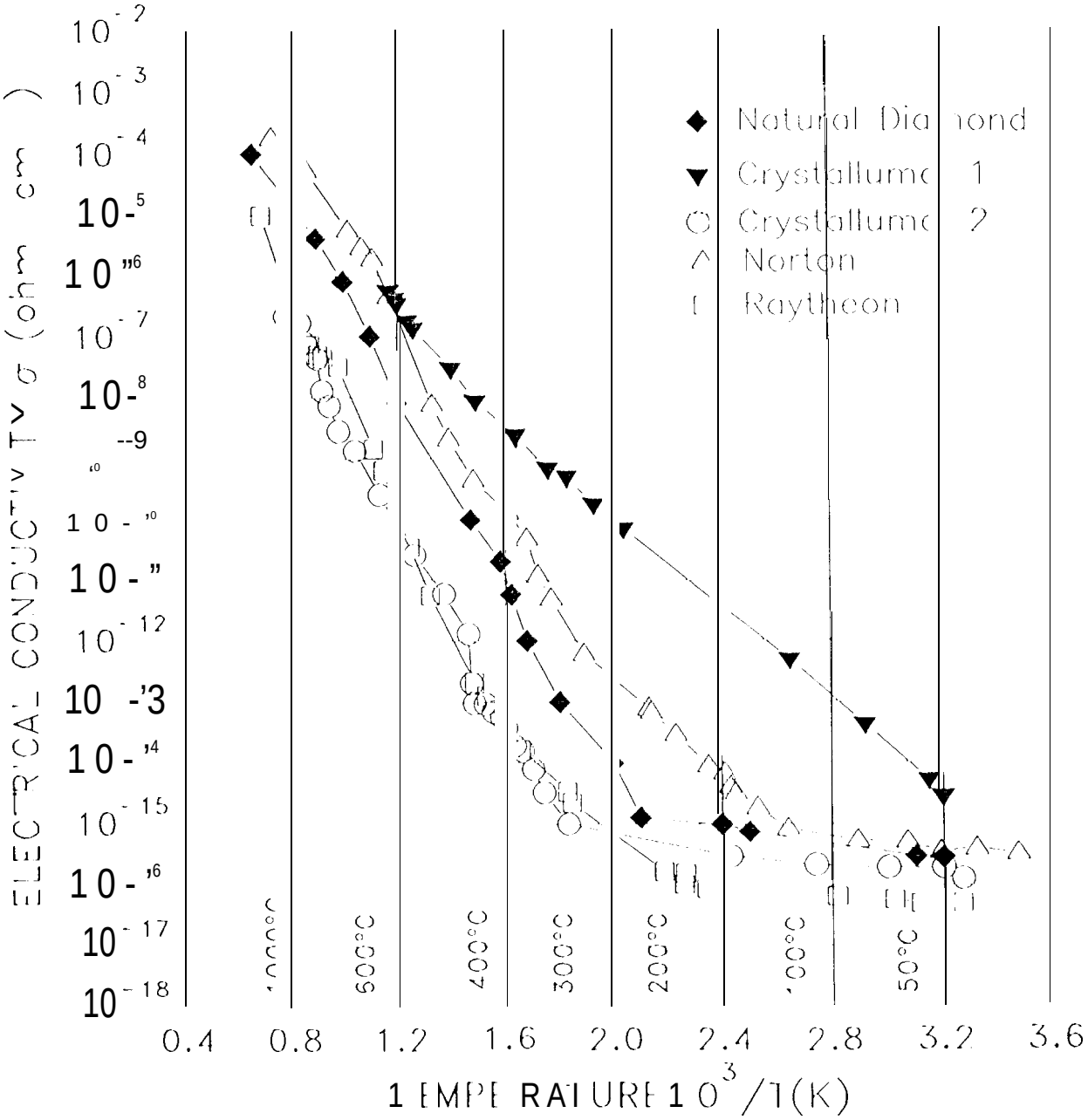
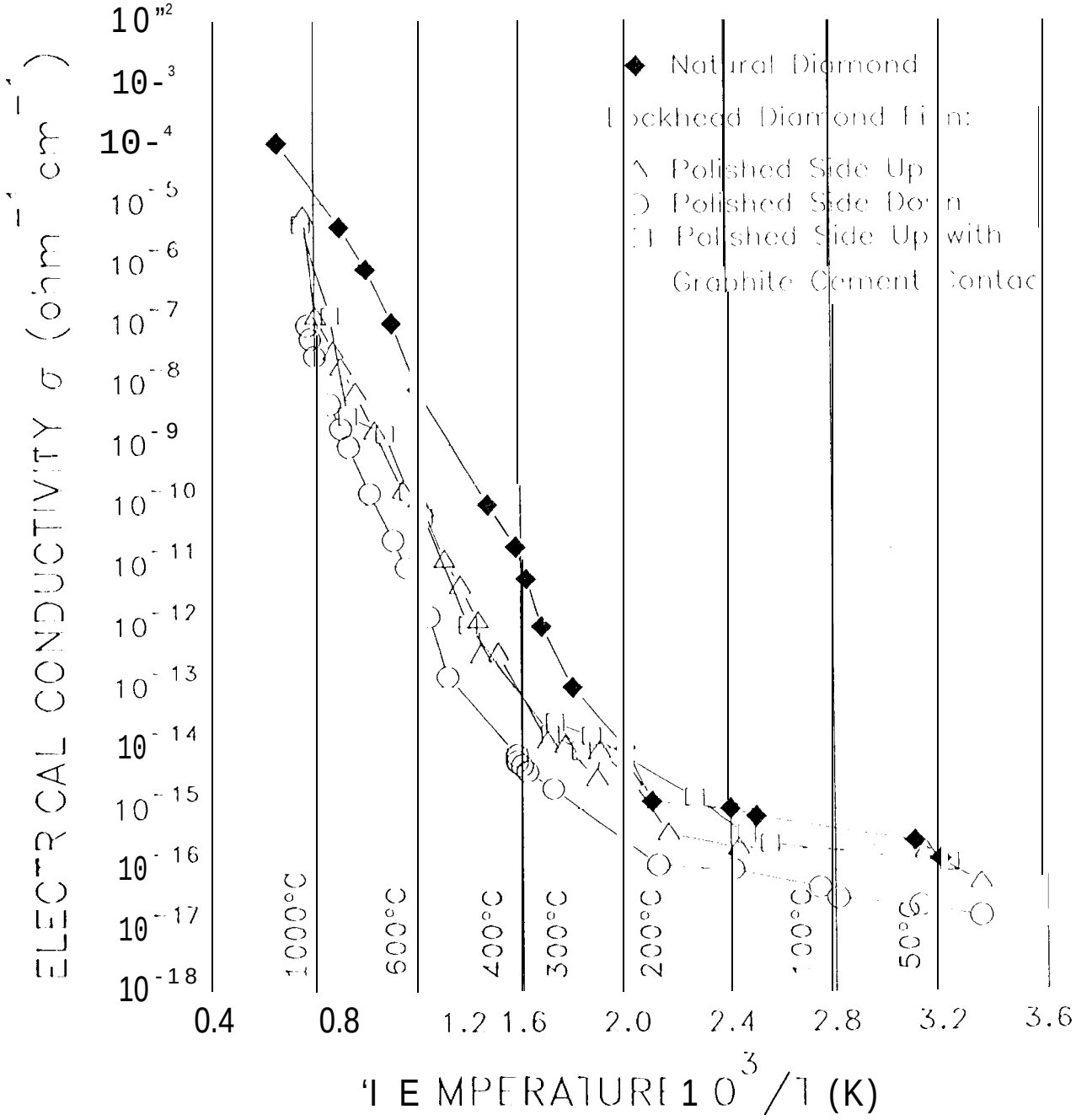
FIGURE CAPTIONS

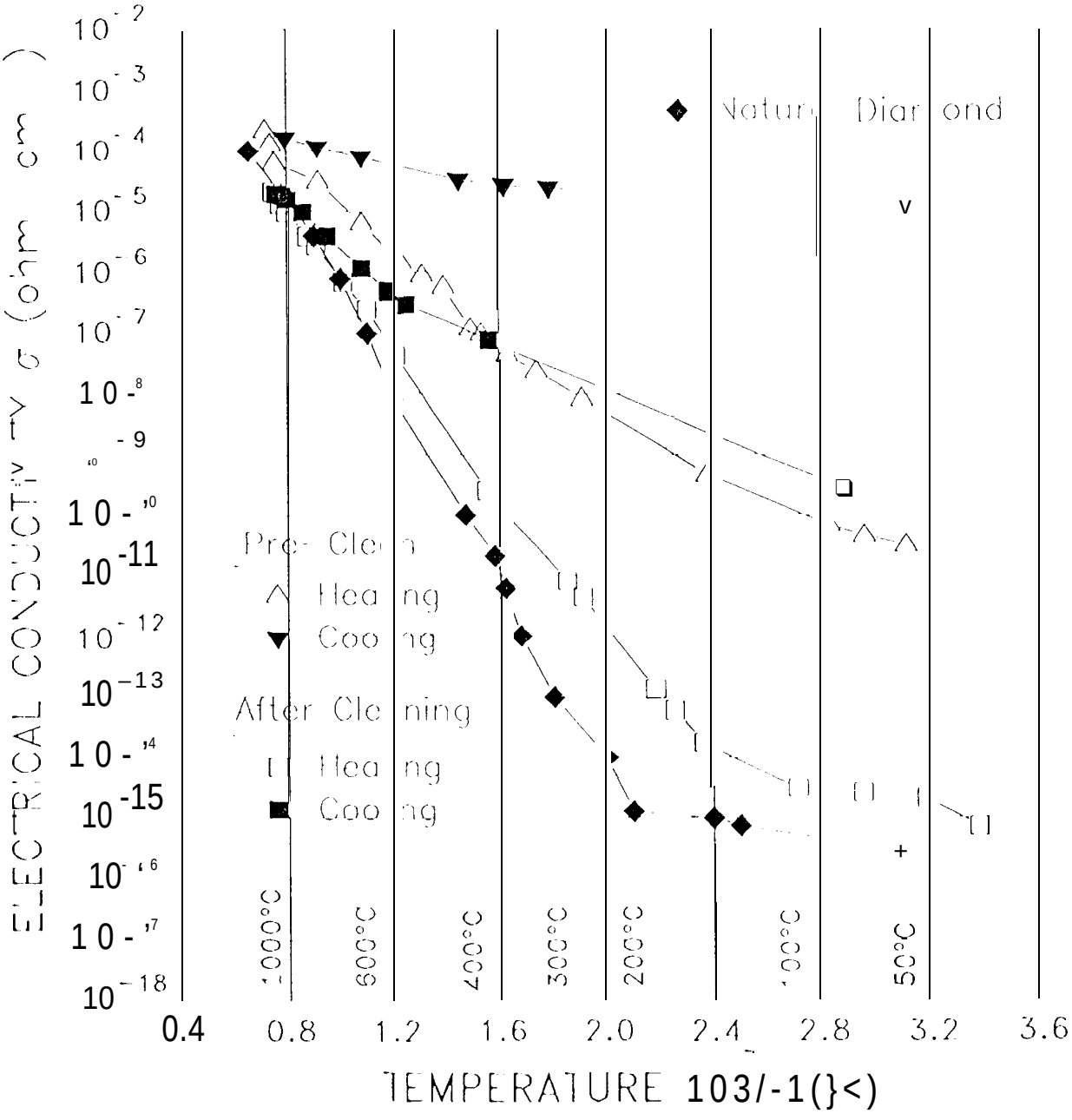
Figure 1. Electrical conductivity plotted as a function of reciprocal temperature for four diamond films: Crystallume-1, 6 μm thick on Si, Crystallume-2, free standing 300 μm thick, Norton, free standing 1.1 mm thick, and Raytheon, free standing 660 μm thick. The conductivity of a natural type IIa diamond is also shown. The conductivities at room temperature are the "apparatus-limited" values. Two of the samples have a conductivity lower than that for natural diamond over the whole temperature range, indicating that they have less defects so are purer than natural diamond.

Figure 2. Electrical conductivity plotted as a function of reciprocal temperature for a free standing Lockheed diamond film 80 μm thick. Data for a natural type IIa diamond are also shown. The conductivity was measured with the polished side up, the rough side up, and with a graphite cement contact instead of the usual Ir foil contact. The conductivities were all lower than that for the natural diamond indicating that the diamond film sample has less defects and so is purer.

Figure 3. Electrical conductivity plotted as a function of reciprocal temperature for a free standing Norton diamond film 1.1mm thick. Data for a natural type IIa diamond are also shown. The conductivity of the film with a "dirty" surface (contaminants and non-diamond carbon) was found to be at least four orders of magnitude greater than that for the film with a cleaned surface.


ELECTRICAL CONDUCTIVITY σ (ohm⁻¹ cm⁻¹)
10⁻²
10⁻³
10⁻⁴
10-⁵
10⁻⁶
10⁻⁷
10-⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
10⁻¹⁸
Natural Diamond
Crystallume 1
Crystallume 2
Norton
Raytheon
600°C
400°C
300°C
200°C
100°C
50°C
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
TEMPERATURE 10³/T(K)


ELECTRICAL CONDUCTIVITY σ (ohm⁻¹ cm⁻¹)
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
10⁻¹⁸
Natural Diamond
Lockheed Diamond Film:
Polished Side Up
Polished Side Down
Polished Side Up with
Graphite Cement Contac
1000°C
600°C
400°C
300°C
200°C
100°C
50°C
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
TEMPERATURE 10³/T (K)


ELECTRICAL CONDUCTIVITY σ (ohm⁻¹ cm⁻¹)
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
10⁻¹⁸
Natural Diamond
Pre-Cleaning
Heating
Cooling
After Cleaning
Heating
Cooling
1000°C
600°C
400°C
300°C
200°C
100°C
50°C
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
TEMPERATURE 10³/T(°K)