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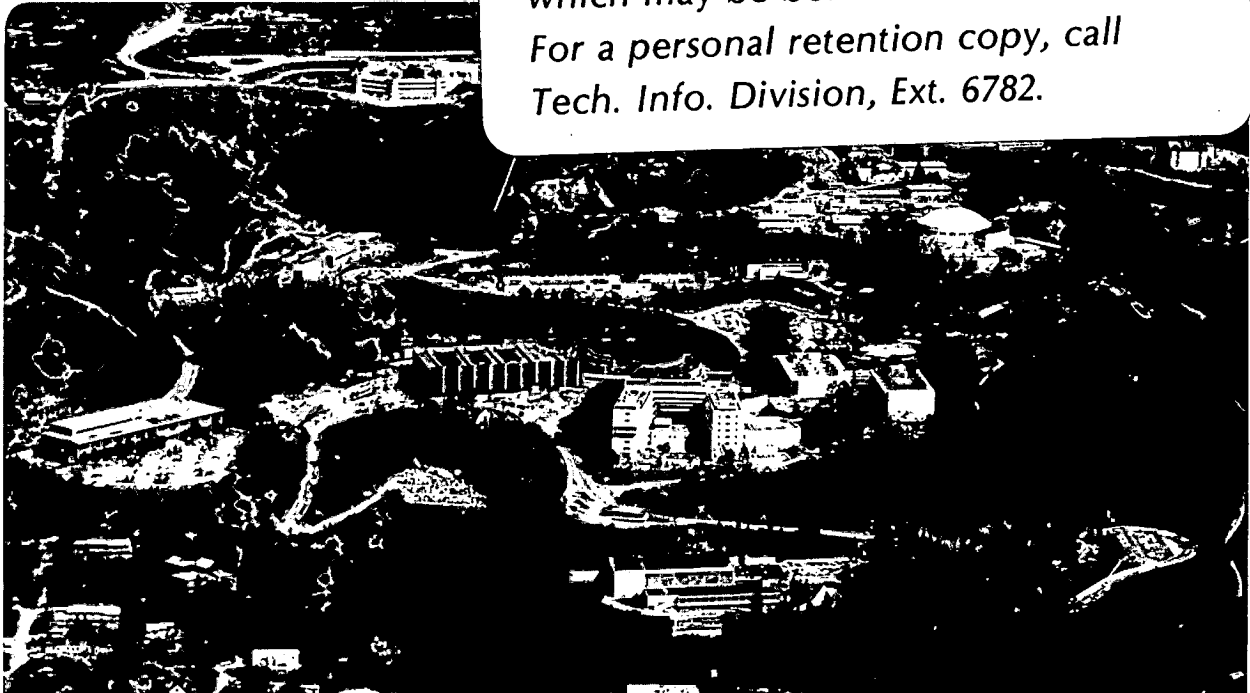
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DISLOCATIONS IN GERMANIUM: EFFECTS OF PLASMA HYDROGENATION*

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DISLOCATIONS IN GERMANIUM: EFFECTS OF PLASMA HYDROGENATION

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Several recent studies have dealt with the deep level states associated with dislocations in silicon^{1,2} and germanium³. Generally the dislocations in silicon are introduced by compression or bending at temperatures $> 650^{\circ}\text{C}$ ^{1,2}. The advantage of using ultra-pure germanium ($N_A - N_D < 5 \times 10^{10} \text{cm}^{-3}$) is that such deformation is not required in order to observe the electrical effects of the dislocations³. Indeed, the effects of fewer than 10^4cm^{-2} dislocations in germanium can be observed using deep level transient spectroscopy (DLTS)¹⁴ measurements. This is important as recent evidence has been presented that the electrical levels measured in silicon are not due to bonding rearrangements associated with the dislocations, but are related to such localized defect phenomena as chemical impurities or vacancies⁵. Obviously in the very pure and undeformed germanium, these latter effects will be minimized.

The effects of exposing dislocated samples to a low pressure hydrogen plasma have also been reported recently. In deformed silicon, a reduction in electrical activity due to the dislocations as measured by DLTS was observed². In undeformed silicon and germanium, it was noted that the physical size of the dislocations was reduced after hydrogenation⁶. Furthermore, in dislocated germanium samples, the hydrogenation treatment produced surfaces containing the smooth shallow etch pits ascribed to hydrogen precipitation⁷. This effect was previously observed only in dislocation-free material, where there

are no nucleation sites for excess hydrogen⁷. This present work investigates the effects on electrical activity of exposing undeformed, ultra-pure germanium samples containing $\sim 10^4 \text{cm}^{-2}$ dislocations to various plasmas.

The samples used were cut perpendicular to the axis of crystal growth, either [113] or [100], and the dislocations counted by using the preferential etch treatments described by Hubbard and Haller³. Two of the three crystals were grown in a H_2 atmosphere and the third in a N_2 atmosphere. The details of the crystal growth conditions have been described previously³. The sample diodes for DLTS were fabricated by implanting ^{11}B to one face and ^{31}P to the opposite face. After an appropriate annealing cycle⁸, this produced thin, stable p^+ and n^+ contacts, respectively. The final sample dimensions were typically $6 \times 6 \times 2 \text{mm}^3$. Figure 1(a) shows the DLTS spectrum recorded for samples taken from a crystal grown in the [100] direction under a H_2 atmosphere, and containing $\sim 2 \times 10^4 \text{cm}^{-2}$ dislocations. Figure 2(a) shows the DLTS spectrum obtained from samples taken from a crystal grown in the [100] direction under N_2 and containing a similar dislocation density. The sharp peak is due to a level of copper, and the underlying broad feature due to the dislocations³. Figure 3(a) displays the capacitance transient spectrum of a sample taken from a crystal grown in the [113] direction under a H_2 atmosphere. The implications of the differences in the spectral features recorded from these samples have been discussed previously³; the electrical-ly active concentrations were determined there by Hall effect.

Plasmas were created within a quartz tube by exciting flowing (0.1 Torr) hydrogen, deuterium or helium with a 300 W, 27 MHz source. Samples were

treated to 600°C for three hours by placement on a high-purity graphite susceptor, to which 550 kHz RF power was coupled. Exposure to un-ionized gases was done in the same apparatus under the same conditions, except no plasma was excited.

DLTS spectra recorded after the heat treatments in molecular hydrogen, deuterium or helium showed no significant changes in the concentrations of the electrical levels associated with the dislocations in any of the three different types of samples. Heating in a plasma of helium also had no apparent effect on the electrical activity of the dislocations—this is shown for the [100], H₂-grown material in Fig. 1(b). Heating in either the hydrogen or deuterium plasmas, however, caused significant reductions in the deep level concentrations associated with the dislocations as evidenced by Figs. 1(c), 2(b) and 3(b). These spectra were recorded at a reverse bias of 1 V, corresponding to a depletion depth of ~ 300 μm. The atomic hydrogen or deuterium appeared equally effective in neutralizing the electrical levels associated with the dislocations, as expected. It is possible that the passivation mechanism is satisfaction of dangling bonds associated with the dislocations. Recently, Pakulis et al⁹ have presented EPR results that lithium ions can also attach to dangling bonds in dislocated, ultra-pure germanium, as predicted by Reiss et al¹⁰. However, we cannot rule out the possibility that the hydrogen, by binding to the dislocation, reduces the surrounding lattice strain, and that it is this reduction in strain we are observing with DLTS. Another possibility of course, is that even in this very pure germanium, the observed defect states are due to chemical impurities complexing with the dislocations, and that we are not measuring the electrical activity due to the dangling bonds of the dislocations themselves.

The result that a helium plasma exposure does not neutralize the electrical levels observed by DLTS is an important one. The difference between heating a sample in a plasma, and in the molecular species of a gas is not simply that between atomic vs. molecular species. The plasma-exposed samples are subject to a high level of ultra violet illumination and particle bombardment, which are not present in the molecular gas treatments. Using a helium plasma, therefore, recreates these conditions without having any atomic hydrogen or deuterium present; this fact, taken together with the results from the samples heat treated in molecular H_2 or D_2 , points to the incorporation of the atomic species as being responsible for the observed passivation effect.

In conclusion, we report the passivation by atomic hydrogen and deuterium of electrical levels associated with dislocations in ultra-pure germanium. This passivation effect is not seen in samples heated in a helium plasma, or in molecular hydrogen or deuterium.

The authors acknowledge the assistance of Jim Duffy, who performed the ion implantations, and the advice of Paul Luke in annealing these samples. The interest and encouragement of Eugene Haller is also appreciated.

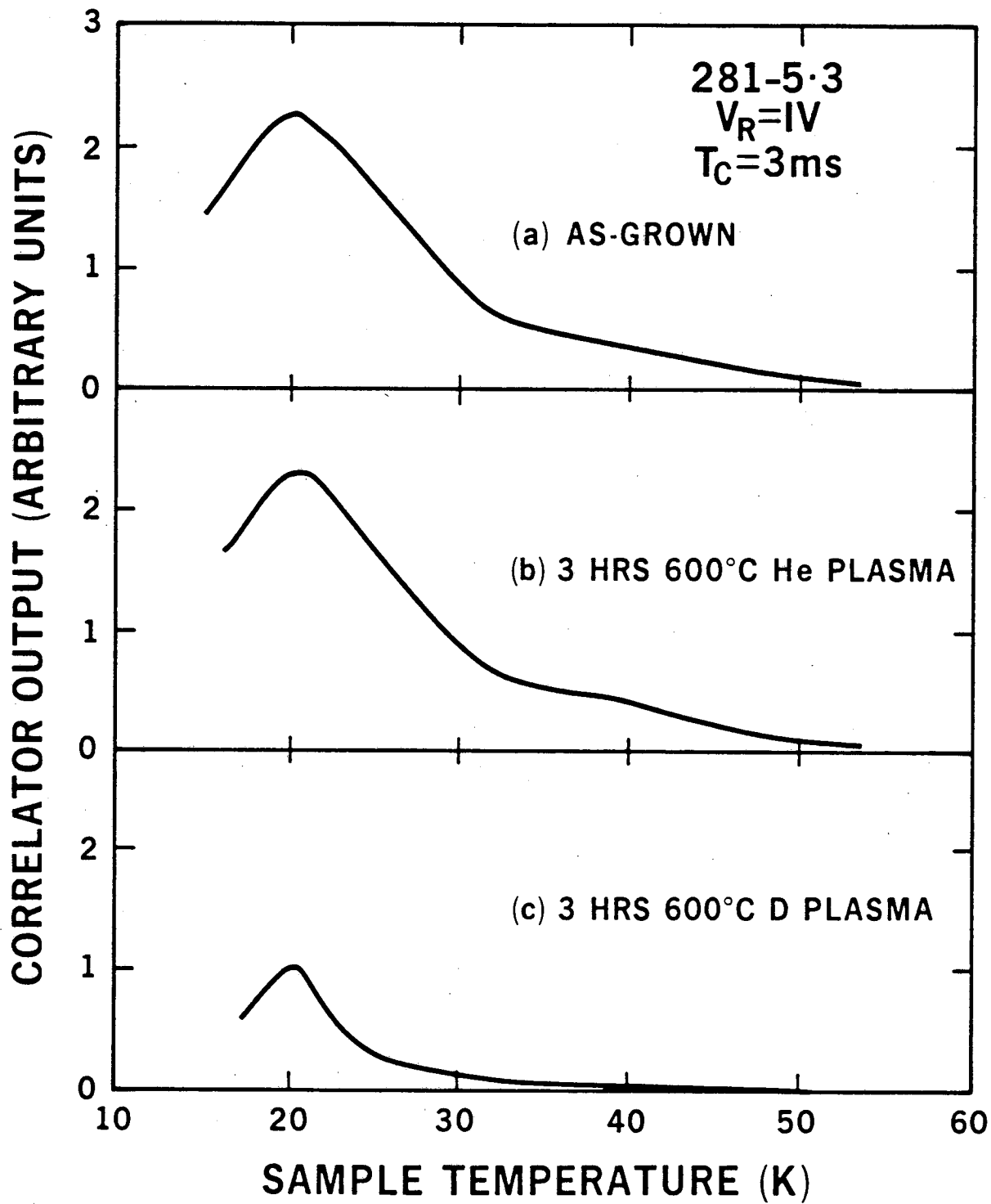
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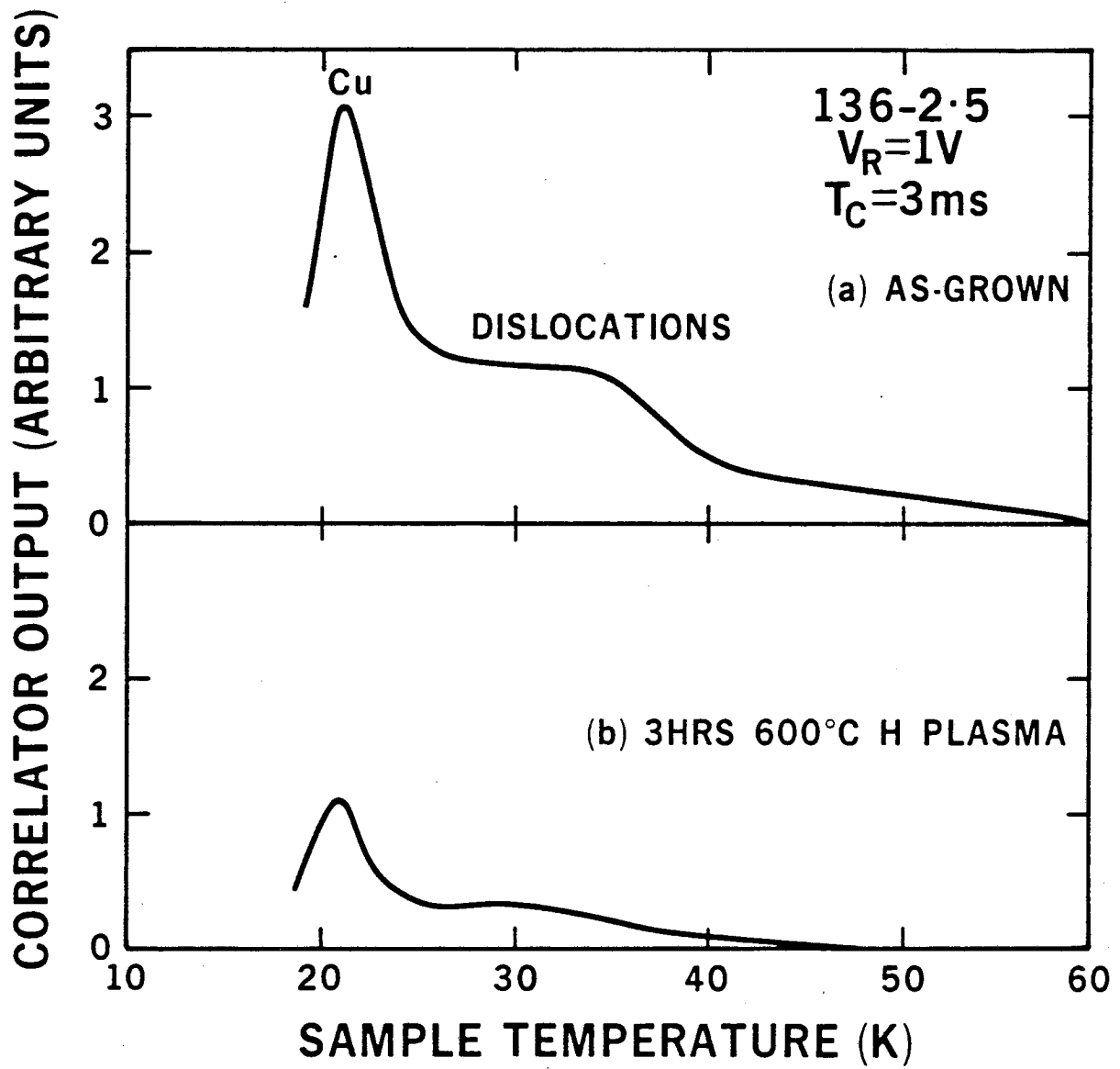
FIGURE CAPTIONS

1. DLTS spectra recorded under the same conditions (reverse bias 1 V, correlator time constant 3 msec) for defect states associated with dislocations in ultra-pure germanium (a) as-grown in the [100] direction, under 1 atm of H₂. Net acceptor concentration $\sim 2 \times 10^{10} \text{cm}^{-3}$, deep level defect concentration $\sim 3 \times 10^9 \text{cm}^{-3}$ for a dislocation density of $\sim 2 \times 10^4 \text{cm}^{-2}$; (b) after heating for three hours at 600°C in a 0.1 Torr helium plasma. Note there is no change in defect state concentration; and (c) after heating for three hours at 600°C in a 0.1 Torr deuterium plasma—a reduction in electrical activity of the dislocation-related defect states is evident.
2. DLTS spectra recorded under the same conditions as Fig. 1 for (a) as-grown ultra-pure germanium, grown in the [100] direction under 1 atm of N₂. Net acceptor concentration $\sim 5 \times 10^{10} \text{cm}^{-3}$, deep level concentration $\sim 4 \times 10^9 \text{cm}^{-3}$ for a dislocation density of $\sim 2 \times 10^4 \text{cm}^{-2}$. The sharp feature is due to copper impurities; and (b) after heating for three hours at 600°C in a 0.1 Torr hydrogen plasma, showing reductions in deep level activity. No effect had been seen after heating in molecular hydrogen.
3. DLTS spectra recorded under the same conditions as Figs. 1 and 2 for (a) germanium grown in the [113] direction under 1 atm of H₂. Net acceptor concentration $\sim 4 \times 10^{10} \text{cm}^{-3}$, deep level concentration $\sim 4 \times 10^9 \text{cm}^{-3}$ for a dislocation density of $\sim 2 \times 10^4 \text{cm}^{-2}$; and (b) after heating for three hours at 600°C in a 0.1 Torr deuterium plasma, showing reduction in deep level electrical activity. No effect had been seen after heating in molecular deuterium.



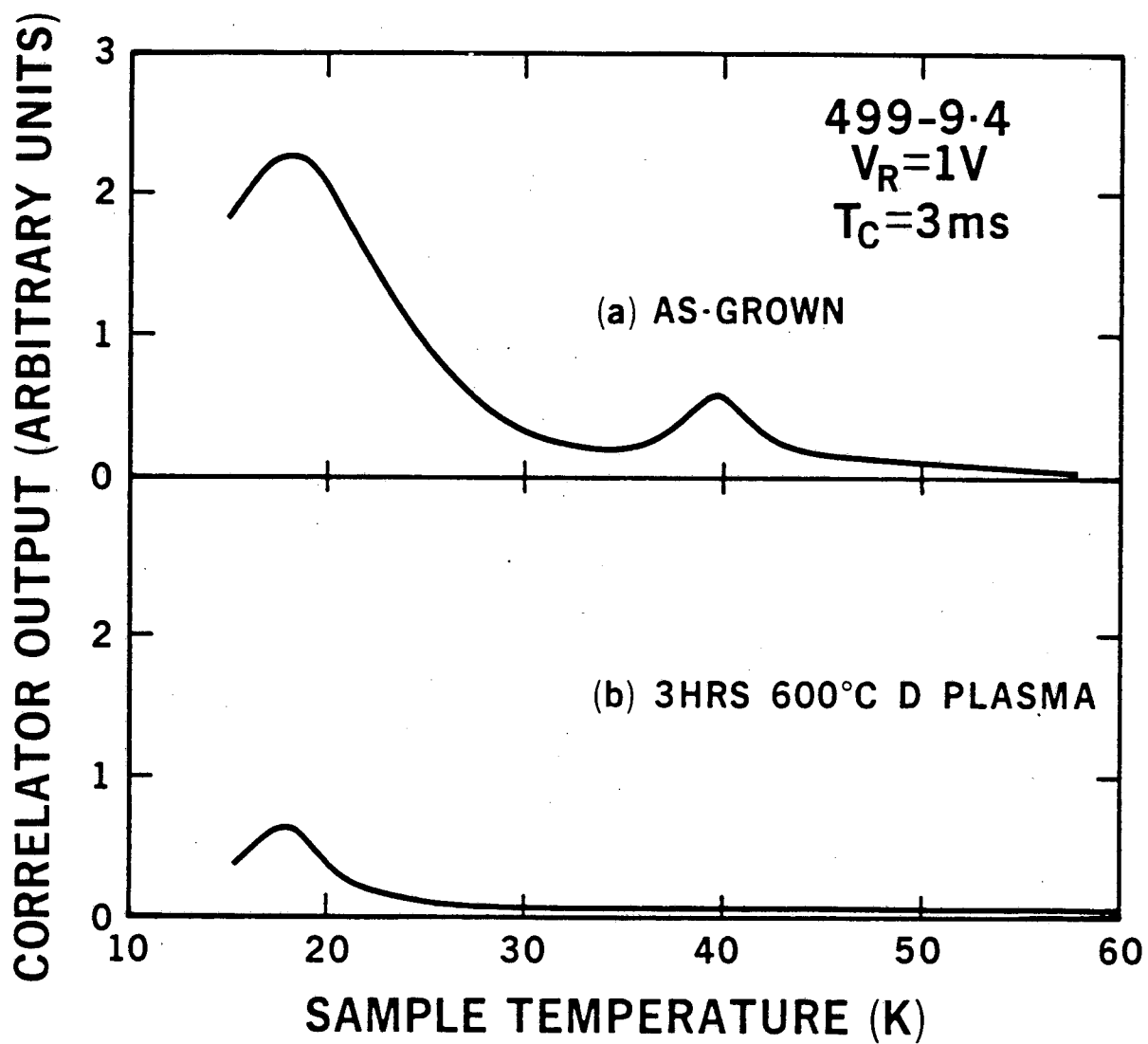
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Fig. 1



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Fig. 2



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Fig. 3

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