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APPLICATION OF TUNNELING TO ACTIVE DIODES

General Electric Company
Advanced Semiconductor Laboratory
Syracuse, New York

Scientific Report No. 7b

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OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
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Abstract

Further aspects of the relationship between injection and trapping and noise effects in GaAs tunnel diodes are presented. Data are presented on several diodes, primarily, however, on a diode exhibiting noise near the Esaki component of current.

An epitaxially grown GaP n, semi-insulating, n structure is described which appears to conduct by means of space-charge-limited emission, and which at higher voltages exhibits high sensitivity to visible light.

Exploratory work on a GaAs pnpn four-layer device is described. The processes employed in this work, i.e. epitaxial crystal growth, diffusion, and evaporation and alloying, are discussed.

I. Trapping Effects and Excess Noise in GaAs Tunnel Diodes

In our previous reports (4-b, March, 1961; 5-b, July, 1961; and 6-b, October, 1961) we described the general features of the trapping phenomena which are observed in GaAs tunnel diodes. As was mentioned, at low temperatures - once the tunnel diodes have been driven into the injection region - a large change can be observed in the I-V characteristics of certain units. Presumably injected carriers undergo Hall-Shockley-Read transitions into trap states and either change the space charge width (junction width), change the population of gap states (to which tunneling occurs) directly, or change the population of gap states (and tunneling to gap states) because of interactions with other trap states affected by Hall-Shockley-Read processes. Although the exact mechanisms responsible for these effects are not well understood, considerable evidence indicates they are in large part due to contaminating impurities such as Au, Cu, Mn, etc. Also, structural defects such as vacancies appear to contribute to these effects. For example, p-type germanium-doped GaAs, which may have a rather large vacancy density, exhibits the effects described above more strongly than does more conventionally prepared and doped GaAs.

We have pointed out previously that it seems likely that the same mechanisms which produce trapping effects and changes in tunnel diode I-V characteristics with injection also are responsible for generation of excess noise. We have been able to fabricate GaAs tunnel diodes in which C. S. Kim has been able to measure essentially only shot noise and little or no excess (1/f) noise. We have utilized completely similar techniques (alloying temperature-cycle, pellet mounting, etc.) but have introduced into the junction-alloy material contaminating impurities and have gotten very noisy diodes. Or, in some cases, by using alloys and techniques that gave low noise diodes on normal pellet material, we have gotten strong trapping and noisy diodes in material thought to have structural defects.

Figure 1 shows I-V characteristic changes produced by minority carrier injection and trapping in a number of different types of GaAs tunnel diodes. The diodes of Fig. 1 are all similar in the sense that all were made on p+ GaAs doped with Ge. Figure 1-a) shows a unit, constructed with a Sn-S alloy dot, which exhibits a strong shift in the Esaki current as a result of injection and trapping. The lower part of Fig. 2 shows the I-V characteristics of the same unit. At 78°K, as bias voltage is first applied to the unit, the peak current is somewhat less than 2 ma. After heavy injection, however, the peak current is almost doubled, (Fig. 1-a), and becomes larger than its room temperature value. The upper part of Fig. 2 shows a plot of noise equivalent current which is seen to be located, in voltage, in the same region as the I-V characteristic changes. The noise current (excess) is over 1000 times greater than that expected of shot noise. The noise observed and I-V characteristic changes are thought to be due to structural defects in the substrate crystal. The position of the levels associated with these effects has not been established. It appears, however, that, according to Hall's original postulation, changing the charge in these levels by injection and Hall-Shockley-Read transitions may have the effect of changing the space charge width (and tunneling current); and perhaps population of gap states (if there are any) near the band edges.

Just to add to the confusion in understanding these effects, we have included Fig. 1-c) which shows I-V characteristic changes (at room temperature) as a result of injection and trapping in a GaAs tunnel diode which is similar to that which provided the data of Fig. 1-a). In this latter unit there are obviously a wide distribution of trapping and gap states, again probably because of structural imperfections.

Figure 1-b) shows trapping data on a unit similar to that of Fig. 1-a) except a Au-Ge dot was alloyed onto the p+ Ge-doped GaAs substrate. At low temperatures, as increasing bias voltage is applied to the diode a conventional tunnel diode I-V characteristic is first observed. However, after injection a very significant hump is produced in the negative resistance region. In this region between 0.2 and 0.3 volts the current change is frequently over 100 %. All units of this construction have been observed to exhibit this type of behavior. Also, we have observed similar effects in certain units prepared by alloying Au-Ge dots on Zn-doped GaAs. The behavior shown in Fig. 1-b) seems to be characteristic of Au-Ge alloyed dots and suggests that Au introduces levels within several tenths of a volt of the conduction band, provided it may be assumed that not much gold diffuses into the p-type substrate crystal and introduce no levels there. The shallow gap-state Au levels to which tunneling occurs and which lead to the hump current do not appear until deeper gold levels are filled (or emptied) by injection. The fact that in diodes of this type injection and trapping effects produce relatively slight change in the Esaki component of current is taken as evidence that Au gap states are exposed to tunneling rather than any change occurring in junction width due to injection and trapping.

Noise measurements on diodes of the type indicated by Fig. 1-b) yield results different than those of the diodes described by Fig. 1-a) and Fig. 2. Instead of the excess noise appearing largest near the region of greatest I-V characteristic change, appreciable noise (room temperature) begins to appear beyond 0.2 to 0.3 volts and increases steadily with voltage. This noise is apparently due to fluctuations of charge into and out of deep Au trap levels. Apparently the levels which contribute the hump current (0.2 to 0.3 volts, Fig. 1-a) are not particularly strong contributors of noise, or do not play a significant role until deeper Au levels are charged.

II. Halogen Vapor Transport and Epitaxial Growth of a GaP N-S.I.-N Structure

In numerous previous reports (2-b, October, 1960; 3-b, December, 1960; 4-b, March, 1961; 5-b, July, 1961; and 6-b, October, 1961) we have described halogen vapor transport and epitaxial growth of semiconductor compounds, e.g. GaAs, GaP, and $GaAs_xP_{1-x}$, by means of closed-tube processes employing metal halides (chlorides), iodine, or free chlorine. In this section we should like to report some further activity in this area of work involving the growth of GaP N+, semi-insulating, N+ structures.

A typical N+-S.I.-N+ structure is shown in Fig. 3-a. The lower N+ region was grown via $SnCl_2$ transport with the GaP source-end of the reaction vessel held at 1100°C and the seed end of the reaction vessel held at 750°C. A $\langle 111 \rangle$ GaAs substrate was used to seed and obtain $\langle 111 \rangle$ epitaxial growth of n-type GaP. The middle S.I. region was grown in the same manner, however with $CuCl_2$ transport and doping. The S.I. layer probed neutral and appeared orange or reddish. The upper n-type region was grown by repeating the process used for the lower n-type region. After each growth process the surface of the epitaxially grown region indicated mild pyramids typical of the $\langle 111 \rangle$ seed orientation. Previous x-ray analysis of similar layers has in all cases indicated epitaxial growth. When the metallurgical section shown in Fig. 3-a is examined in strong light, the middle S.I. region as expected appears orange or reddish.

Structures of the type shown in Fig. 3-a have been mounted on headers as diodes and exhibit the electrical characteristics shown in Fig. 3-b. The diode whose characteristics are shown in

Fig. 3-b was not etched and was roughly 0.1 x 0.1 cm^2 in area. Out to voltages approaching 100 these diodes have tended to be very high impedance (low leakage currents) and appear to conduct by space charge limited emission. When light is shined on the diodes, a change in current is observed which increases with voltage and becomes at higher voltages orders of magnitude higher than the dark current. If it is assumed that these are indeed space charge limited emission currents, light apparently changes the current drastically by changing the charge state of traps. These effects require further study but suggest that these diodes may be useful for radiation study or as radiation counters. We should remark that the true sensitivity of these diodes is not evident in Fig. 3-b since the heavily doped N+ outer regions of the diode shield the S.I. region from illumination.

Further work is planned with these structures.

III. GaAs PNPN Switch

The purpose of this activity is to explore the feasibility of making a GaAs pnpn switch of inherent high speed capability. Initially a simple two-terminal device is our objective, and if successful, would lead ultimately to 3-terminal devices of higher degrees of sophistication.

Our present approach to these objectives consists of the following:

1) Deposit epitaxially a thin n-type base on heavily-doped p-type GaAs substrate material. The epitaxial layer should have a relatively low doping level and a rather high degree of perfection so that 1) carriers can be injected into and transported through it and 2) other regions and junctions can be formed in it.
2) Diffuse a shallow p-type base region into the n-type epitaxial layer.
3) Evaporate and alloy (or perhaps diffuse or grow epitaxially) an n-type region, and thus an emitter junction, on the shallow p-type base region.

A. Epitaxial growth of GaAs

The major effort has been directed towards forming a suitable n-type epitaxial base layer on p-type seeds. Both closed tube and open tube techniques have been employed, with the open tube process being favored for reasons of convenience and simplicity as well as apparently better control of uniformity and thickness of the epitaxial layers. The open tube technique depends, just as the closed tube technique, upon well-known metal-halide disproportionation reactions. In our work hydrogen chloride has been used as the transport agent with hydrogen introduced as a carrier gas. H Cl concentration in the gas stream has been approximately 0.5 mole %. Poly-crystalline n-type GaAs (10^{16} - 10^{17} donor atoms/cm^3) has been used as the source and single crystal Cd or Zn-doped GaAs has been used as substrate or seed crystal. The deposition apparatus consisted of a two zone furnace with a quartz reaction tube. Gas purification and drying apparatus were employed to insure good quality gases. Separate quartz holders for seed and source crystals were provided, and were such that they could be conveniently introduced or withdrawn from their respective temperature zones. A temperature difference of approximately 100°C has been employed between source and seed. Temperatures of 800°C to 900°C and 700°C to 800°C have been used for respectively the source and the seed.

The rate of epitaxial growth depends upon seed crystal orientation, and appears to depend significantly upon H Cl concentration in the carrier gas (hydrogen) as well as the extent of contact between the carrier gas and source for a given set of temperature conditions. A reproducible growth rate of 0.6 micron per minute has been achieved on substrates with $\langle 111 \rangle$ orientation. Substrates oriented in the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions gave higher growth rates than those oriented in the $\langle 111 \rangle$ direction. The $\langle 110 \rangle$ and $\langle 112 \rangle$ growth directions also yielded better thickness uniformity as compared to the $\langle 111 \rangle$ direction. Typical epitaxial surface structures which have been obtained are shown in Fig. 4. The growth rate of the epitaxial layer on the "A" or "B" face of a $\langle 111 \rangle$ oriented seed did not appear to be significantly different. X-ray transmission measurements taken on $\langle 111 \rangle$, $\langle 110 \rangle$, and $\langle 112 \rangle$ wafers with thick epitaxial layers showed no lattice distortion or twinning.

The epitaxial layers grown as described above have been predominantly n-type with carrier concentrations of the order of $10^{18}/cm^3$ in spite of the fact that source crystals have been lightly doped n-type ($\sim 10^{16}$ to $10^{17}/cm^3$). This doping level is somewhat high for the requirements of the proposed pnpn switch. Hence, an attempt is now being made to decrease the doping level and simultaneously increase carrier mobility.

B. P-type base diffusion

All diffusions for the switch p-type base have been carried out in evacuated quartz ampoules. Free Zn was first tried as the diffusant, but although it could be easily controlled in penetration and uniformity across the area of the wafer, it was abandoned because of problems with excessively high doping level. Zn-Ga alloys diffusion sources resulted in more lightly doped diffused regions but also gave undesirable increases in the length of time of the diffusion cycle to give a given diffusion depth.

Manganese has been investigated as an alternate choice of diffusant. The diffusivity of Mn in GaAs is quite high, even at a temperature of 750°C. Nevertheless with Mn one can obtain low surface concentrations ($\sim 10^{18}/cm^3$). Several trial Mn diffusion runs have been made on n-type material doped to 10^{17} atoms/cm^3. Junction depths were as shown below:

Diffusion time, minutes	Diffusion temp., °C	Junction depth, microns
120	796	21
30	750	3
20	793	3.8

In experiments with epitaxial wafers, free Mn has been sealed in an evacuated ampoule ($\sim 5 \times 10^{-6}$ mm Hg) with the GaAs wafer and an excess of crushed GaAs. After heating the ampoule is air quenched and yields a wafer with its epitaxial layer maintaining its initial shiny appearance. Trial diffusion runs have given uniform junction depths but so far have not been found adequate for pnpn switches (perhaps because of problems in the epitaxial layers).

C. Evaporation and alloying of n-type emitter regions

In this phase of the effort to build a pnpn switch the major problem has been to form by evaporation and alloying a thin, uniform n-type regrown region in a thin, diffused p-type base region. Several major problems are experienced in attempting this, problems which are not usually encountered in alloying tangential-wetting alloy spheres on GaAs (for example, spheres alloyed on GaAs to form tunnel junctions).

Figure 5-a shows a cross-section of germanium-doped Au-Sb eutectic alloyed on p+ GaAs to form a tunnel junction. The region designated N+ is a thin, uniform n-type GaAs region regrown from the alloy. When alloys such as that shown in Fig. 5-a are evaporated and alloyed into GaAs, serious problems are encountered in wetting the GaAs surface uniformly. As the wetting and alloying temperature is reached the surface tension of the alloy becomes large enough to cause "balling" and localized rather than broad-area alloying. Also, as shown in Fig. 5-b, problems are experienced in obtaining uniform regrowth even when wetting and alloy-attack is uniform.

Figure 5-c shows a cross-section of an alloy system which thus far seems to be most satisfactory. Although it is evident that the regrown region is not of uniform thickness, it does extend from edge to edge under the alloy. Even though no

completely satisfactory alloy system is at hand, the control in this work appears to be sufficient to allow exploratory GaAs pnpn switch work to continue.

By use of epitaxial growth, diffusion, and alloying, we have been able to assemble a four-layer structure. Figure 6-a shows three layers of the structure, i.e. the p-type GaAs substrate, an n-type epitaxial base layer, and a p-type base region diffused into the epitaxial layer. Figure 6-b shows such a structure complete with an n-type alloyed emitter region. Electrically, the unit of Figure 6-b was not operative, probably because of two reasons: 1) the n-type epitaxial base was too thick and 2) the p-type diffused base was doped too heavily. Also, quite possibly the perfection of the epitaxial layer could be questioned, and if so, quite likely minority carrier transport in base regions formed in such material may not be adequate. At this point, however, it is encouraging to be able to form a potentially operative four-layer structure in GaAs.

The individuals who contributed to the work reported are:

Staff	Supporting Staff
N. Holonyak, Jr.	S. F. Bevacqua
S. W. Ing, Jr.	R. E. Morrison
	R. Krohl

Figure Captions

Fig. 1 Injection and trapping I-V characteristic changes in GaAs tunnel diodes: a) Sn-S alloyed on p+ Ge-doped GaAs, b) Au-Ge alloyed on p+ Ge-doped GaAs, and c) Sn-S alloyed on p+ Ge-doped GaAs.

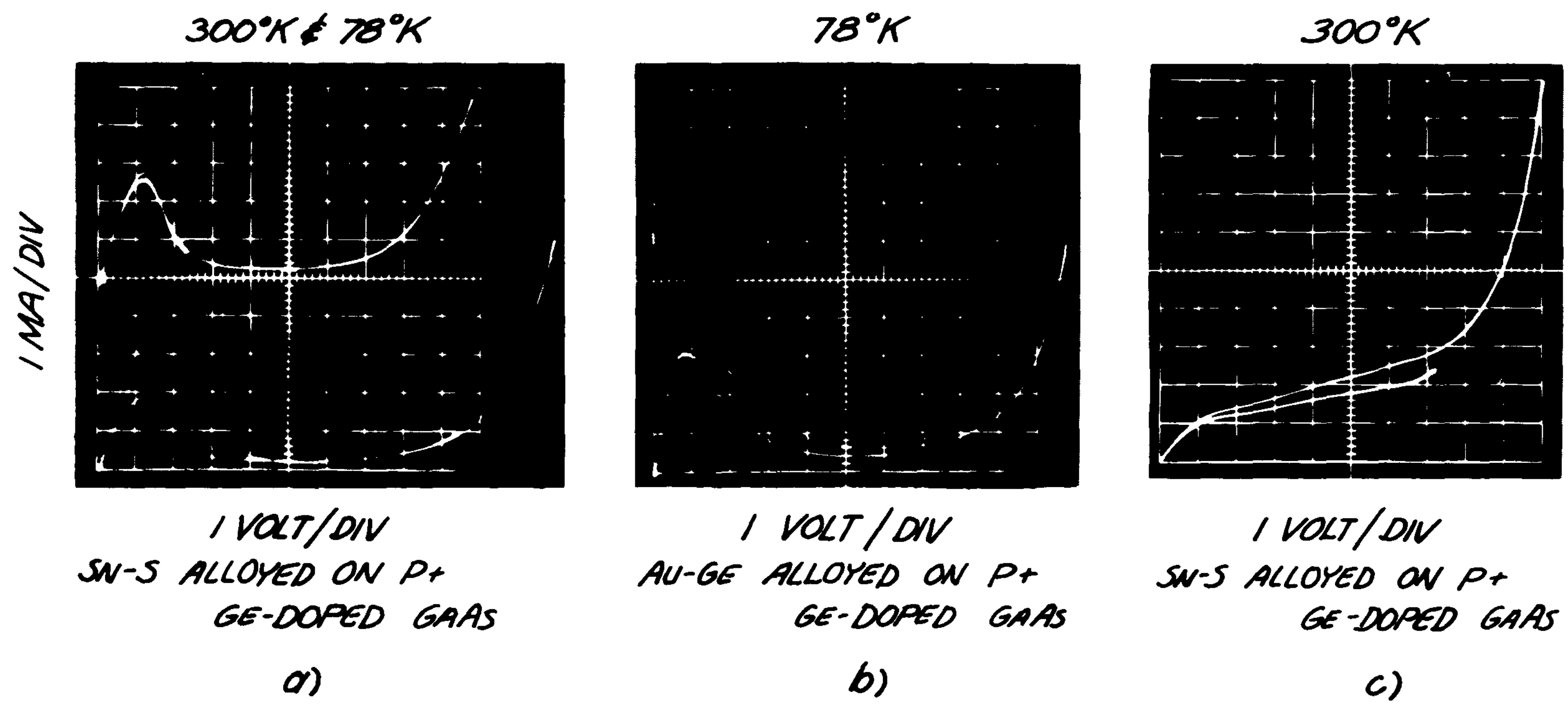
Fig. 2 Injection and trapping I-V characteristic changes and noise in a GaAs tunnel diode; diode Sn-S alloyed on p+ Ge-doped GaAs.

Fig. 3 Epitaxially grown GaP n+, semi-insulating, n+ diode (a), which exhibits space-charge-limited emission and considerable light sensitivity (b).

Fig. 4 N-type GaAs epitaxial surface structure on substrate crystals oriented a) $\langle 111 \rangle$, b) $\langle 110 \rangle$, and c) $\langle 112 \rangle$.

Fig. 5 N-type alloy-regrown regions on p-type GaAs: a) Au-Sb-Ge, b) Au-Sb-Ge-Sn (evaporated), and c) Sn-Ag-Te (evaporated).

Fig. 6 Three-layer (a) and four-layer (b) structures in GaAs.



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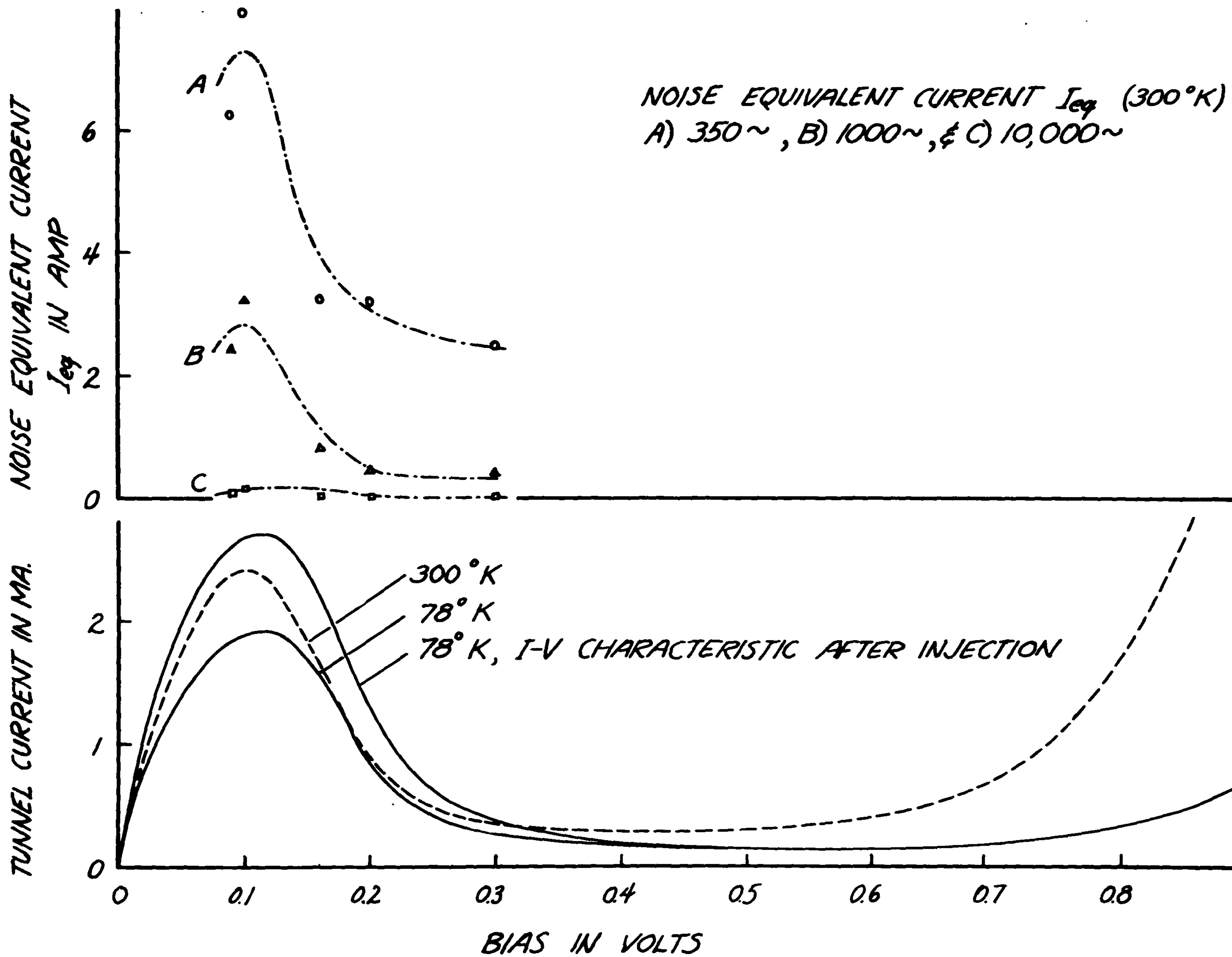

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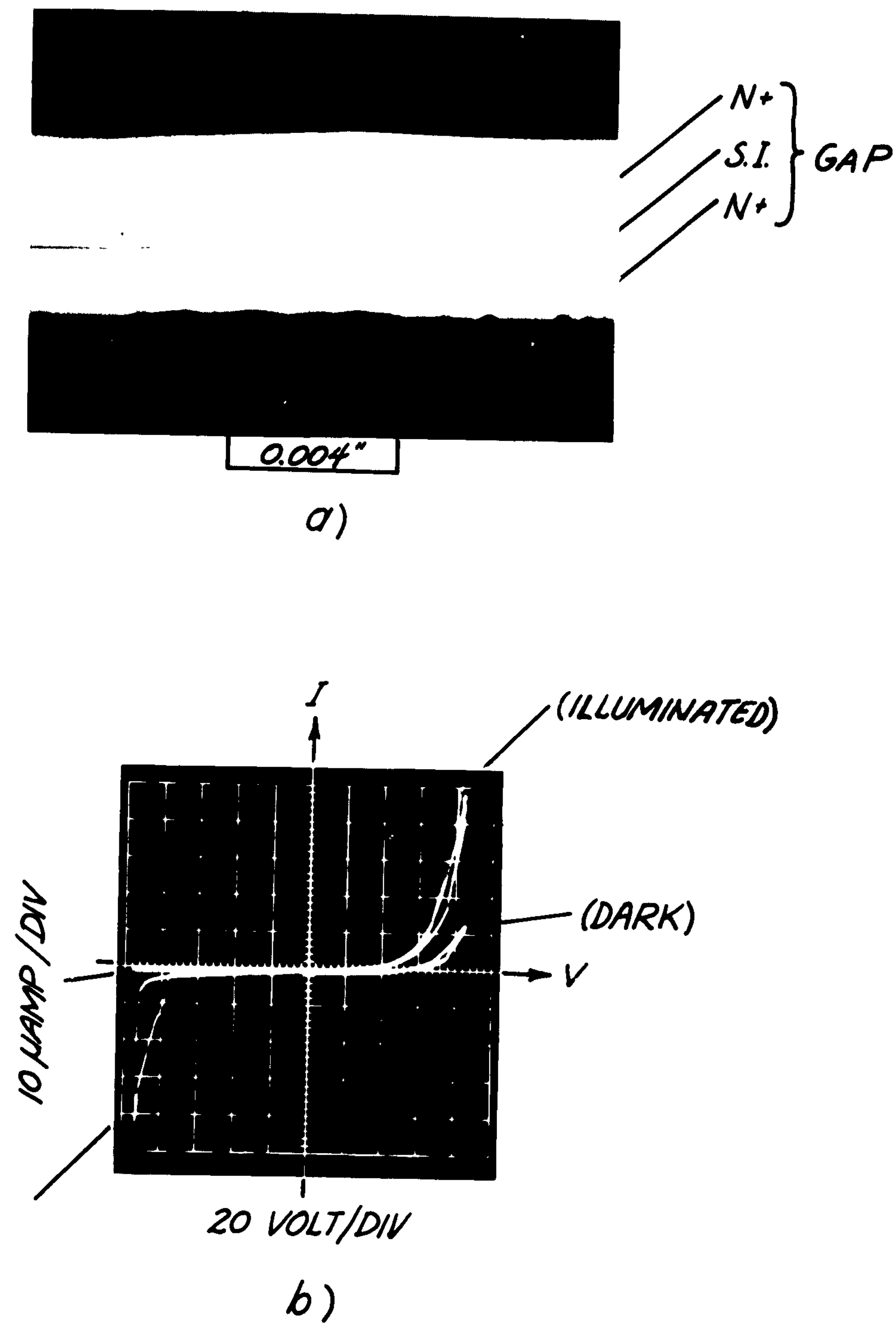

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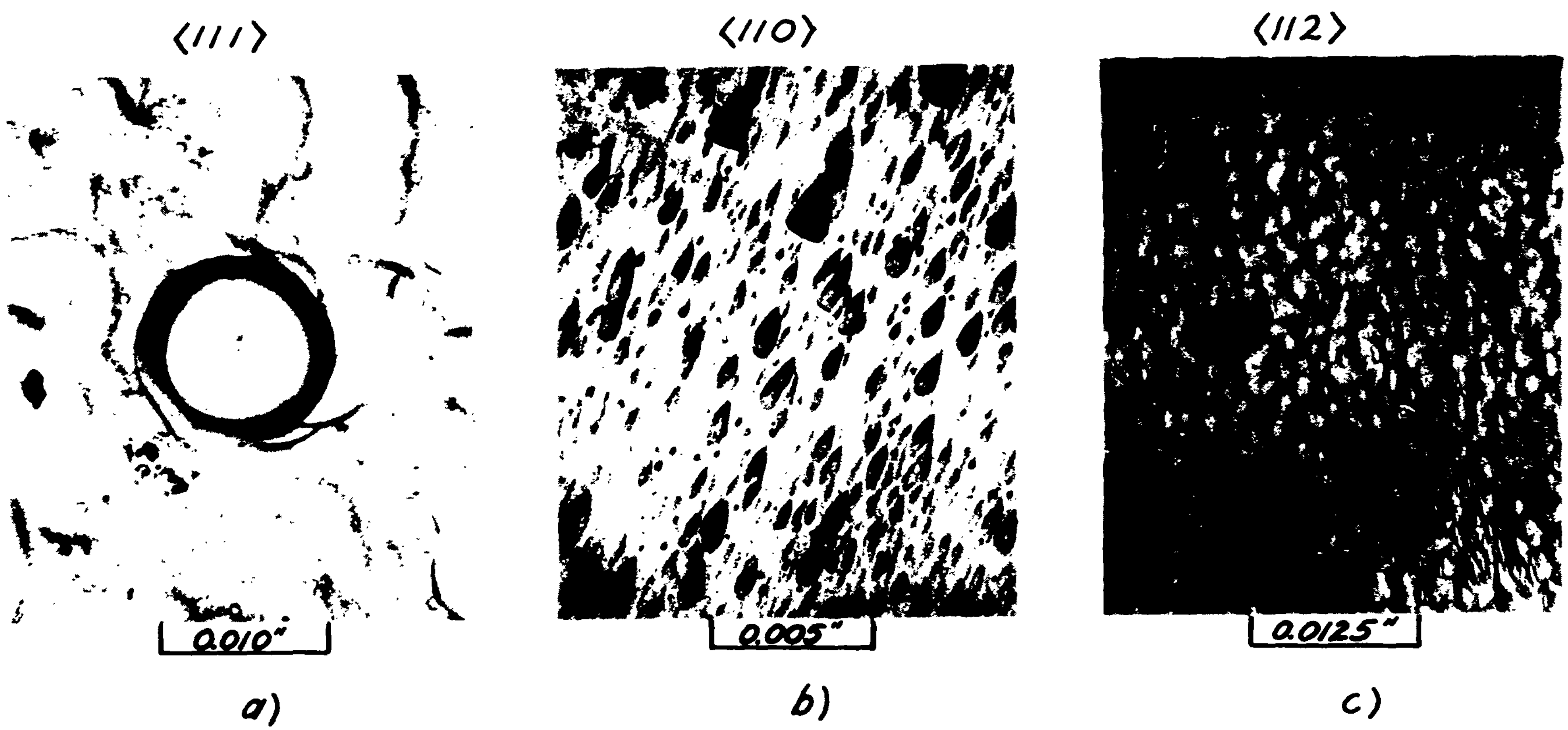
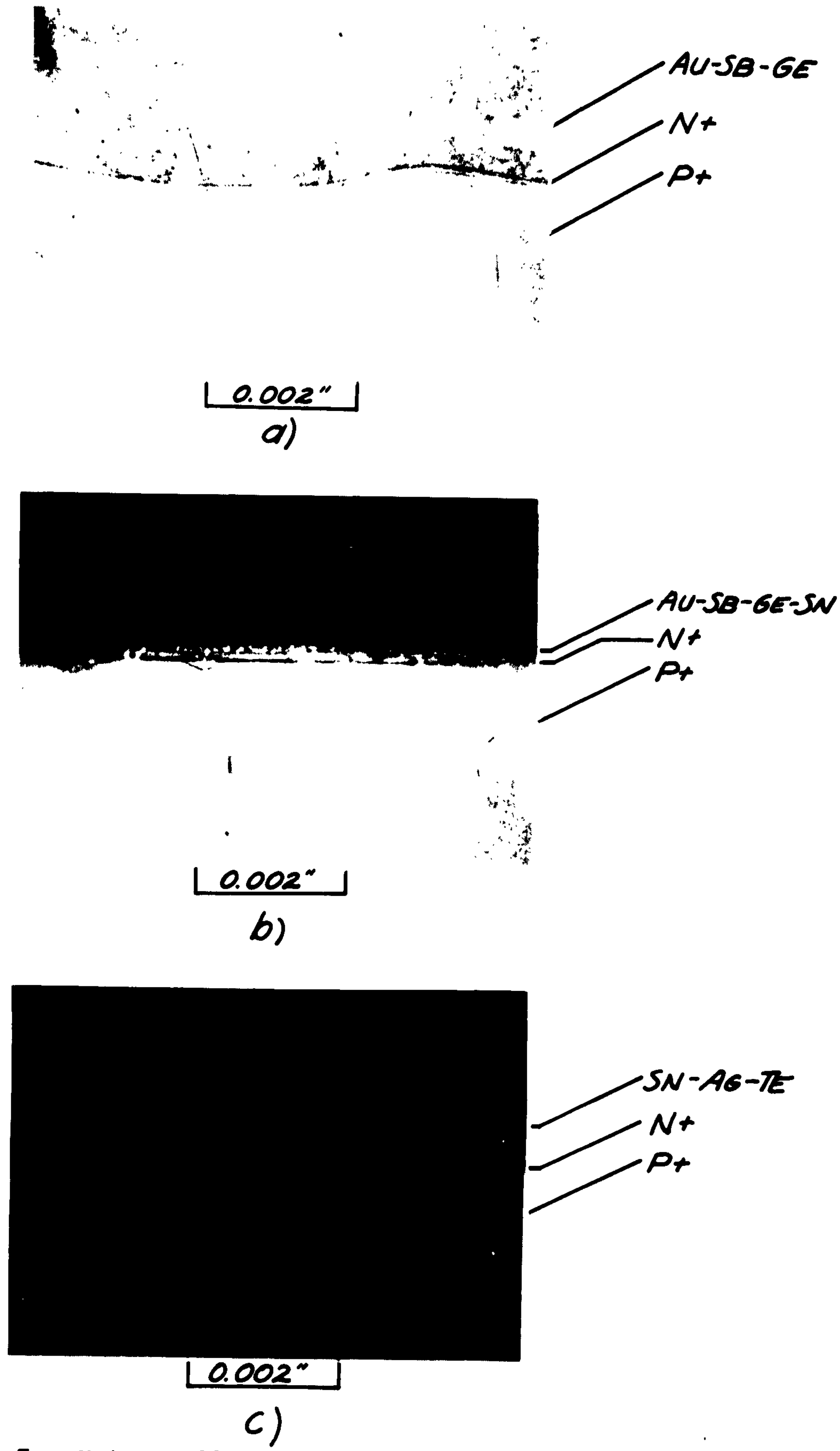


Figure 4 N-type GaAs epitaxial surface structure on substrate crystals oriented a) ⟨111⟩ , b) ⟨110⟩ , and c) ⟨112⟩ .



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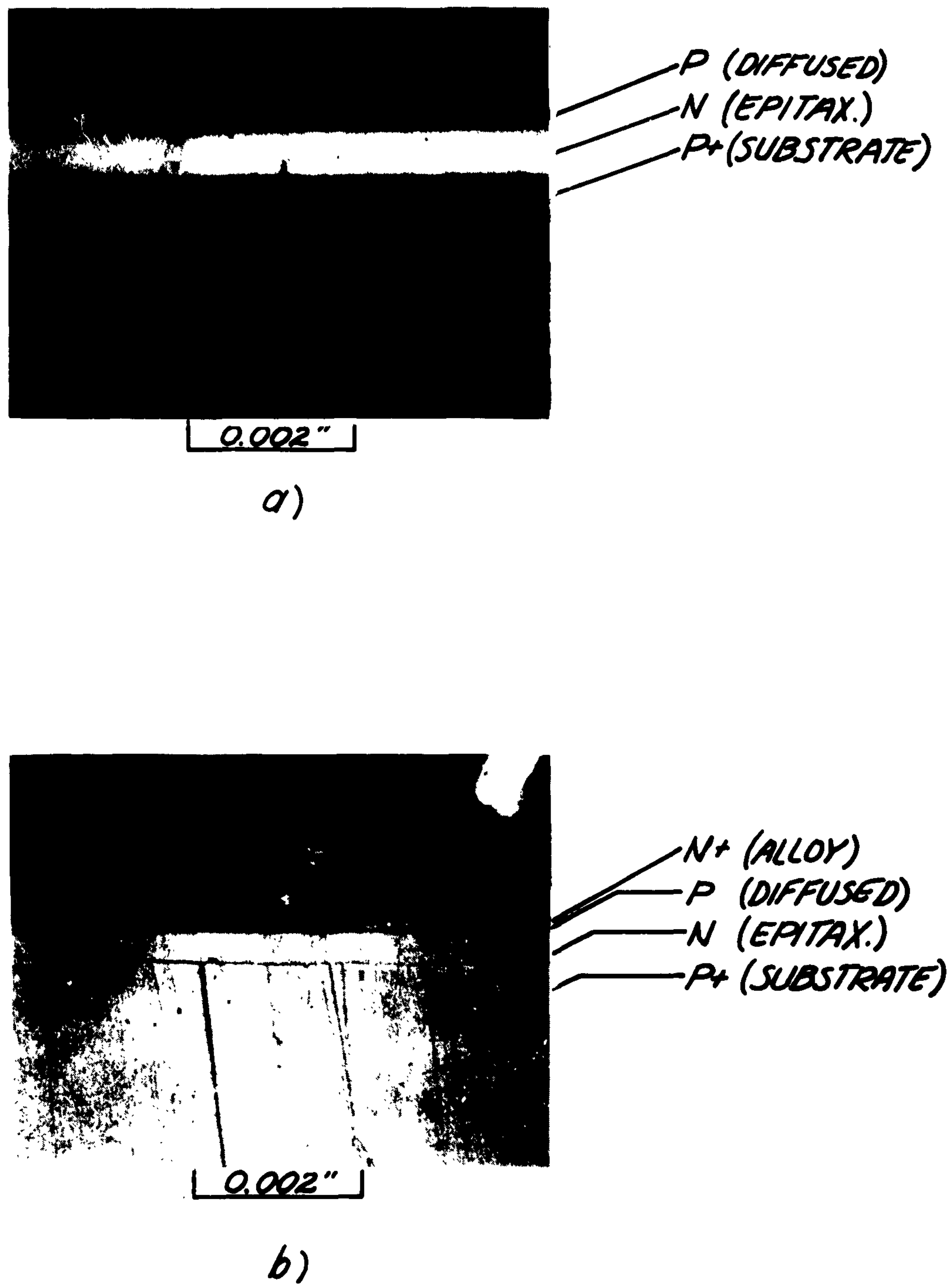

Figure 6 Three-layer (a) and four-layer (b) structures in GaAs.

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