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Growth and Properties of Iron-Doped LPE GaAs Layers

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Abstract

Iron-doped GaAs layers were grown from gallium-melts by the liquid-phase-epitaxy (LPE) technique in order to study the electrical behaviors of iron atoms in LPE materials. A new horizontal LPE growth system with a 'gold furnace' was developed for the purpose. Grown layers showed n-type and p-type conduction, depending on the amount of iron added to the Ga-melt. This indicates the presence of a compensation effect by iron atoms acting as acceptors, and it does not agree with the findnigs of previous works. It was found that iron-doped LPE layers with Schottky contacts, grown on n^+ substrates, exhibit a new current-controlled negative resistance phenomena under certain conditions. In a simple circuit configuration consisting of a series resistor and d.c. power supply, such a diode shows switching and oscillation behaviors. High frequency quasi-sinusoidal oscillations up to several ten megaherz and low-frequency relaxation oscillations with sharp voltage drops are observed, depending on the circuit conditions.

1. Introduction

After more than ten years of development since the first proposal by Nelson in 1963[1], the liquid phase epitaxy technique has now become one of the well-established standard techniques to grow high-quality epitaxial layers of GaAs and the related III-V binary and ternary compound semiconductors in homo- and hetero-junction forms. As is well known, this technique has important applications for fabrication of advanced optoelectronic and microwave devices such as junction lasers, light-emitting diodes, solar cells, Gunn divices and MESFET's.

One of the key problems in the preparation of high-quality epitaxial materials for such applications is the control of the so-called 'deep-level' impurities whose behaviors are often detrimental for operation and reliability of the devices[2]. Additionaly, intentional incorporation of deep level impurities in a controlled fashion can also be useful for formation of semi-insulating layers, buffer layers and new devices based on their behaviors[2].

In spite of such importance, however, only a very limited amount of information is available at present concerning the behaviors of deep-level impurities in LPE materials. One thing which has now become clear at least is that they often behave quite differently in LPE materials from thier behaviours in the bulk materials. Oxygen acts, for instance, as a shallow donor in the LPE case[3,4],

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whereas it is known to be a deep donor in bulk crystals. As for chromium, there are conflicting reports[5–8] in the literature concerning the possibility of obtaining Cr-doped semi-insulating crystals with the LPE technique. Several authors[4,5] asserted that chromium acts as a shallow donor again in LPE layers, enhancing n-type conduction, rather than acting as a deep-acceptor.

The present study was carried out in order to clarify the electrical behaviors of iron atoms incorporated into GaAs by the liquid phase epitaxy technique. In bulk materials, iron is reported to be a deep acceptor having two levels at 0.52 and 0.37 eV from the top of the valence band. In the case of LPE materials, however, Schlachetzki and Salow[6] reported recently that incorporation of iron enhanced n-type conduction. In an apparent contradiction to this observation, there also is a recent report by Lang and Logan[8] in which they observed the presence of a deep acceptor level at 0.52 eV from the valence band edge in LPE layers doped with iron. Thus, there is at present no well-established self-consistent understanding of the behaviors of iron in LPE materials.

The purpose of this report is to present some preliminary results of the efforts to clarify the behaviors of 'deep level' impurities such as iron in LPE material by artificial incorporation of impurities into the melts for growth. A new horizontal carbon slider type LPE growth system was specially developed for the purpose. *n*-type and *p*-types layers were obtained with the same growth procedures, depending on the amount of iron added to the Ga-melts. This clearly indicates the presence of a compensation effect by acceptor-type impurities, and does not agree with the previous observation by Schlachetzki and Salow[6]. Under certain conditions, iron-doped GaAs LPE layers with Schottky top contacts and n^+ substrates underneath are found to exhibits marked S-type negative resistance characteristics. Oscillation and switching phenomena related to the negative resistance are also observed. Two distinctly different modes of oscillation are possible in a simple circuit configuration consisting of a series resistor and a d. c. power supply. One is a high-frequency quasi-sinusoidal oscillation up to several MHz and the other is a low-frequency relaxation oscillation with sharp voltage drops whose fall time is of the order of a few ten nanoseconds. The possible mechanisms for such behaviors are briefly discussed.

2. Liquid Phase Epitaxy System and Growth Procedure

The block diagram of the LPE growth system is shown in Fig. 1. The temperature of the furnace is controlled by a PID temperature controller combined with a linear ramp mV generator for controlled cooling at a constant rate of variable magnitudes. Epitaxial growth is performed in a high-purity hydrogen flow at about 1 atom. pressure and at a flow rate of about 1 litre per min.. A palladium diffusion unit (Johnson Matthey Metals Limited, Model H 5) is used for purification of commercially available hydrogen gas. It is well known that a flat temperature profile and a delicate control of the furnace temperature are crucial factors for good epitaxial growth. From this point of view, a so-called 'gold furnace' with a resistance heater was specially designed and fabricated. In this furnace, a reflecting mirror made of an evaporated gold film of about 1000 Å thickness is deposited over the inner wall of the glass cylinder in order to form a thermal cavity, where a homogeneous radiation equilibrium is easily achieved with a small value of heat capacity. Typical performances of the gold furnace constructed at our laboratory are briefly compared with those of a conven-

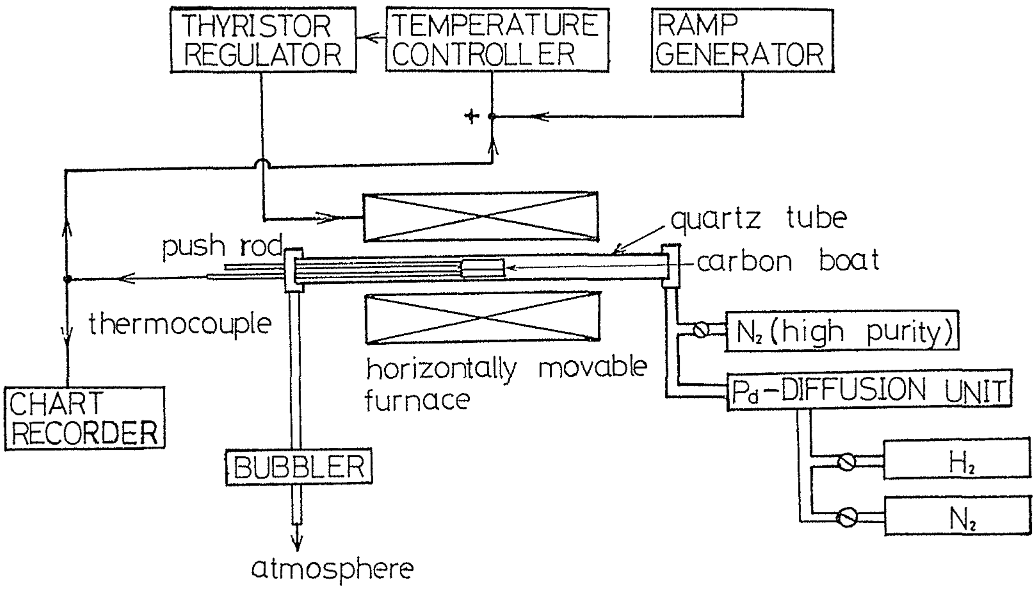

Fig. 1 Block Diagram of LPE Growth System

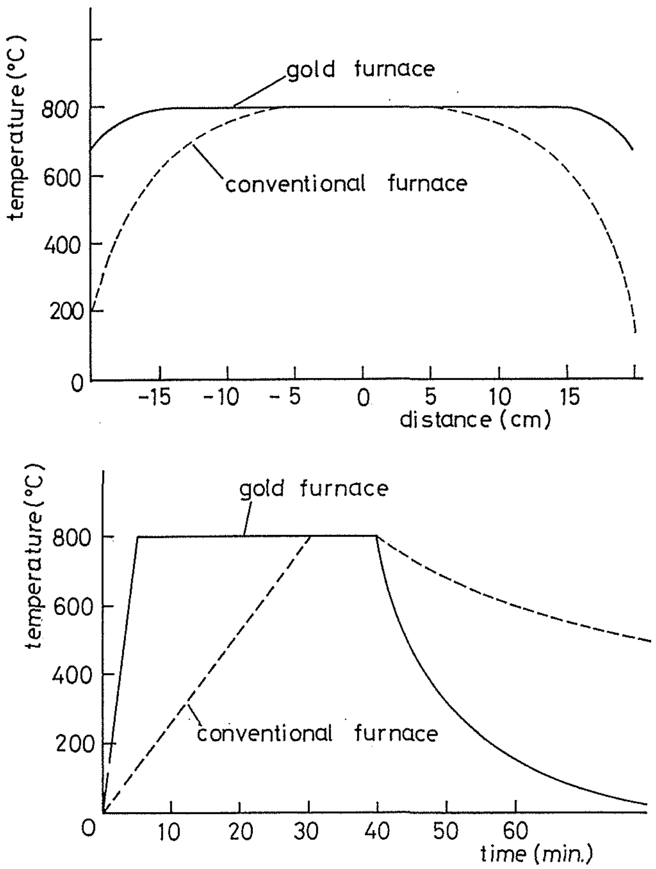

Fig. 2 Performances of Gold Furnace As Compared with That of Conventional Furnace
(a) Temprature Profile (b) Dynamic Behaviors

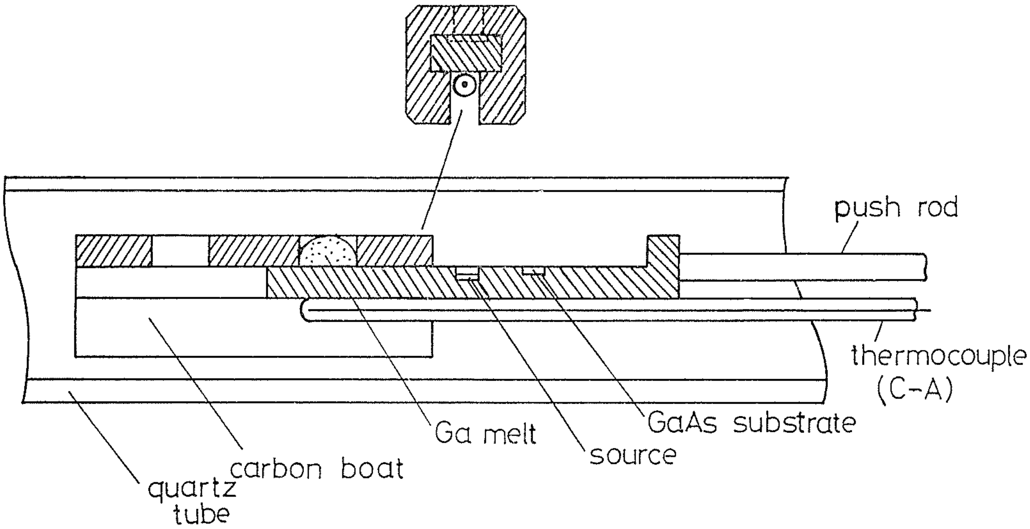

Fig. 3 Carbon Boat Assembly

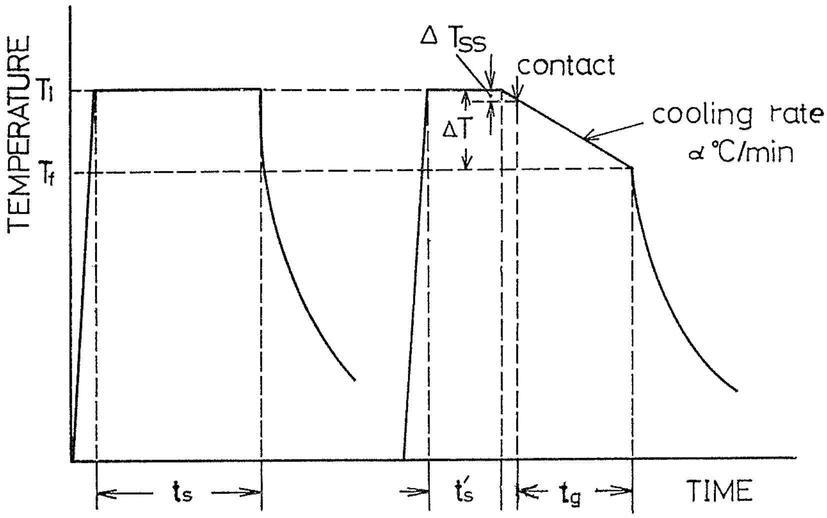

Fig. 4 Temperature Program

tional resistance-heated furnace with asbestos heat insulation, previously used in our laboratory, as shown in Fig. 2 (a) and (b). Both furnaces have the same length of the heating zone (40 cm) and about the same maximum electrical power input (2 kw). Remarkable improvements are seen in the profile and the dynamic characteristics.

The high-purity carbon slider assembly is schematically shown in Fig. 3. As shown in the figure, it has a fairly deep recess to place the source crystal. The standard temperature program of the epitaxial growth cycle is shown in Fig. 4. During the period for saturation denoted by t_s, the gallium-melt which contains approximately such an amount of GaAs as is necessary to saturate the melt at the temperature T_i, is kept in contact with the source crystal in order to establish a true saturation by dissolution or precipitation. The value of t_s was chosen to be 4 hours in the present study. Then, the furnace is cooled down, and the substrate is loaded into the boat assembly. Then the furnace is heated up again, and after the passage of the time required for the reestablishment of saturation, denoted by t_s', controlled cooling of the furnace is initiated at a constant cooling rate of α °C/min.. t_s' of 30 min. and α of 0.5–1.0 were used in the present experiment. When a suitable supersaturation is achieved by the temperature drop ΔT_{ss}, the substrate is moved in to make it in contact with the melt. In this sliding movement, the deep recess for the source crystal takes the bottom tip of the melt away with it, and consequently, a fresh melt surface is expected to come in contact with the substrate. When the temperature reaches T_f, the melt is detached from the substrate by pushing the slider further in, and the furnace is cooled down rapidly.

3. Properties of Grown Epitaxial Layers

The growth conditions and some of the properties of the grown layers are summarized in Tab. 1 and 2 for ten succesful growth runs. As the GaAs source material, undoped polycrystal of n-type conduction with a carrier concentration of 9.0×10^{15} cm^{-3} and a mobility of 4300 cm^2/V•sec (supplied by Mitsubishi Metal Corp.) was used. High purity gallium of 7 nine grade (supplied by Mitsubishi Metal Corp.) was used for the melt. The conventional pre-epitaxy cleaning procedure was applied to each substrate just before it was loaded into the growth system. For iron doping, high-purity iron wire (99.99%) was used. To minimize the possibility of oxidation of iron, the wire was usually stored in vacuum. In general, the surface morphology of the grown layers was good, showing shining mirror-like surfaces. The thickness of the grown layers ranged from 10 to 40 μm. Fig. 5 shows a photograph of the (110) cleavage plane of the iron doped

Table 1

Sample No.	Substrate	Dopant (wt. %)	T_i (°C)	T_f (°C)	ΔT_{ss} (°C)	α (°C/min)	Type	Carrier Concentration (cm^{-3})
701	SI (Cr) (100)	none	800	600	10	1	n	6×10^{15}
702	SI (Cr) (100)	none	800	600	10	1	n	4×10^{15}
1000	n^+ (Si) (100)	Fe 0.2%	800	800	5	1	n	9×10^{14}
1100	n^+ (Si) (100)	Fe 2.0%	800	700	5	0.5	n	5×10^{14}
1200	n^+ (Si) (100)	Fe 3.0%	800	700	5	0.5	n	C–V with severe hysteresis
1300	n^+ (Si) (100)	Fe 5.0%	800	700	5	0.5	Schottky contacts	
1401	n^+ (Si) (100)	Fe 5.0%	800	700	5	0.5	showed S-type negative	
1402	n^+ (Si) (100)	Fe 5.0%	800	700	5	0.5	resistance	

Table 2

Sample No.	Substrate	Dopant (wt. %)	T_i (°C)	T_f (°C)	ΔT_{ss} (°C)	α (°C/min)	Thickness (μm)
1502	SI (Cr-O) (100)	Fe 5.0%	800	700	5	0.5	20
1503	SI (Cr-O) (100)	Fe 5.0%	800	700	5	0.5	5 (polished)

Results of Van Der Pauw Measurements

	Type	Hall Coefficient (cm^3/C)	Carrier Concentration (cm^{-3})	Mobility (cm^2/Vsec)
1502	p	6.3×10^2	1.0×10^{16}	18
1503	p	1.7×10^3	3.7×10^{15}	34

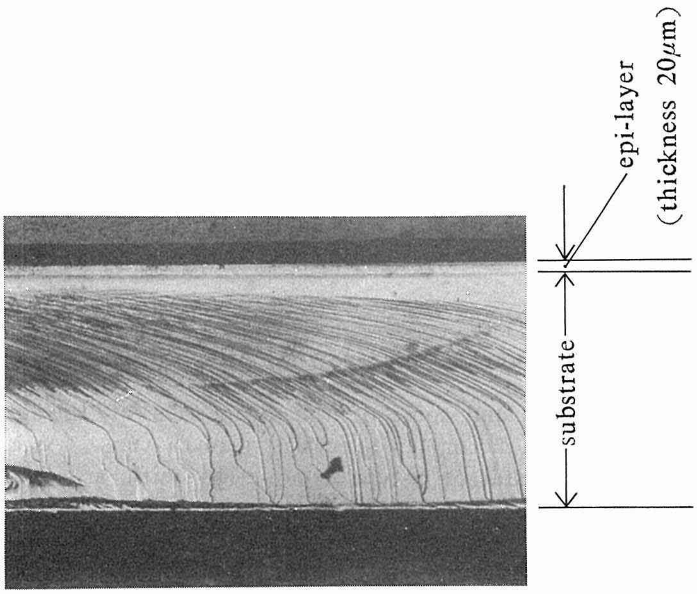

Fig. 5 (110) Cleavage Crossection of Grown Layer

epi-layer. No. 1502, grown on the Cr-O doped semi-insulating substrate. The layer thickness is 20 μm. For the junction delineation, potassium ferricyanide etching solution was used.

As seen in Tab. 1, the undoped layers showed n-type conduction with a carrier concentration of about $5 \times 10^{15}\,cm^{-3}$. The carrier concentration was measured by the Schottky C-V measurement. The above figure could be interpreted as the backgound residual donar level for the present growth system and growth procedure. When the melt was doped with iron to the levels of 0.2–3 wt. %, the grown layers still showed n-type conduction, but the carrier concentrations measured by Schottky C-V method were significantly reduced down into the range of $10^{14}\,cm^{-3}$. The amount of reduction also has a consistent dependency on the amount of iron added to the melt, indicating that iron is acting as a compensating acceptor impurity. This observation does not agree with the recent observation by Schlacktzki and Salow[6] where they reported that iron enhanced n-type conduction. Under the assumption that every incorporated iron atom acts as the compensation acceptor the distribution coefficient should be of the order of $k \simeq 10^{-6}$ in the present case. When the amount of iron was further increased to 5 wt. %, the grown layers on n^+ substrates started to show an entirely different and new characteristic of S-type negative resistance, when Schottky contacts for the carrier concentration measurement were deposited. This result was highly reproducible in three succesive runs with different melts having the same make-up, as indicated in Tab. 1.

Typical current-voltage characteristics of the Schottky diodes on such layers are shown in Fig. 6 (a) and (b). The S-type instability invariably takes place in the direction where the metal electrode is biased positively and the other direction allows much smaller conduction with no instability up to the avavalance break-down voltage. The threshold voltage for the instability ranged from 10 to 30 volts for the diodes with 10 to 40 μm thicknesses. However, no clear relationship was established so far which relates the threshold voltage with the layer thickness.

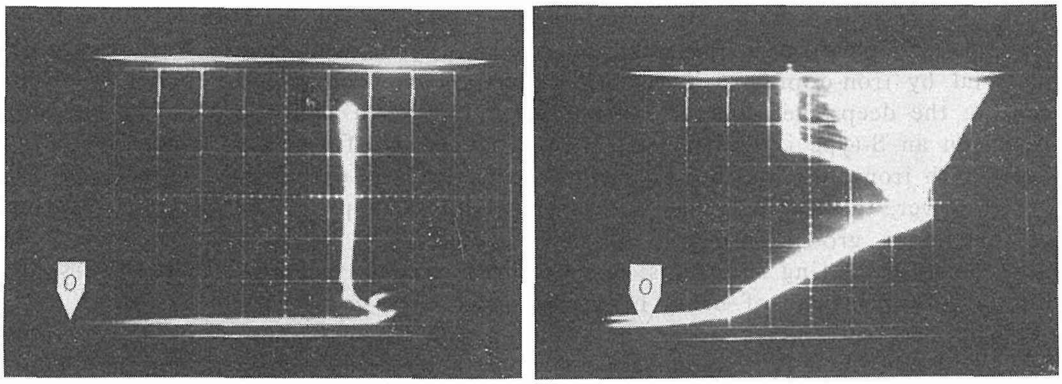

Fig. 6 V-I Characteristic Showing *S*-type Instability
(a) HOR: Voltage, 2 V/cm, VER: Current, 1 mA/cm
(b) HOR: Voltage, 2 V/cm, VER: Curreut, 0.5 mA/cm

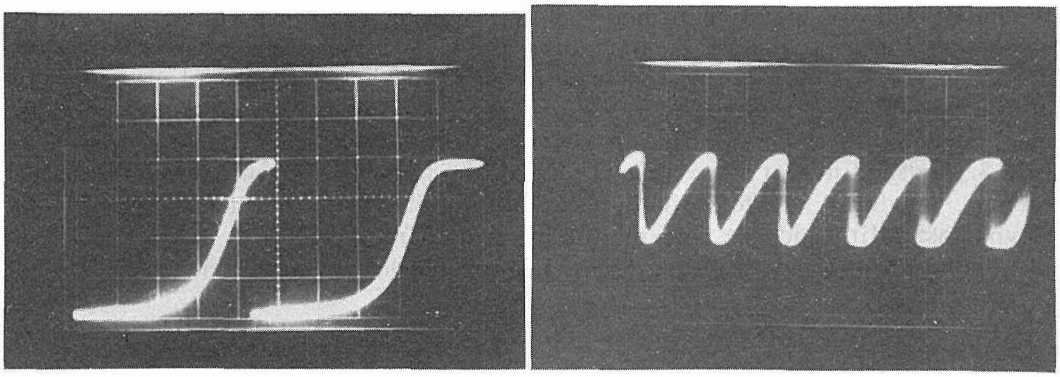

Fig. 7 Voltage Oscillation Waveforms of Diode
(a) Relaxation Oscillation, HOR: 0.2 msec/cm, VER: 5 V/cm
(b) Quasi-sinusoidal Oscillation, HOR: 5 μsec/cm, VER: 1 V/cm

In a simple circuit configuration consisting of a series resistor R_s and a d. c. voltage source with the voltage E_s, the diode shows oscillation and switching phenomena. Fig. 6 (b), for instance, clearly demonstrates the onset of oscillation. Two distinctly different types of oscillation were observed as shown in Fig. 7 (a) and (b). The traces in Fig. 7 are the voltage waveforms across the diode. The low-frequency relaxation oscillation in Fig. 7 (a) was observed when the source voltage is near the threshod, and it corresponds to the 'on-off' cycling of the diode. The period of the cycle increases with the value of the series resistance, suggesting an RC type relaxation oscillation. It is noted that the transition from off- to on- state occurs rapidly with the typical fall time of the voltage waveform being of the order of ten nanoseconds. On the other hand, when the source voltage is high, the diode stays in the on-state and shows a quasi-sinusoidal oscillation as shown in Fig. 7 (b). The oscillation frequency is dependent on the series resistance and the source voltage, and the maximum frequency obtainable appears to be several ten MHz.

The mechanism which seems most probably responsible for the above S-type instability would be the so-called double-injection mechanism[11] into the semi-insulating layer. GaAs *p-i-n* diodes with *i*-layers being prepared by oxygen doping[12] or chromium doping[12,13] into bulk materials are known to exhibit S-type instabilities. The present case has a proper polarity of the metal electrode for such an interpretation, if one considers the possibility of injection of holes from the Schottky electrode. The picture of having a semi-insulating or high resistivity material by iron-doping also fits in the well-known deep-acceptor model of iron, causing the deep-level compensation effect. In fact, a high-speed pulse generator based on an S-type instability has been produced by forming a highly resistive layer with iron-diffusion into bulk GaAs (commercially called the 'Jump Diode')[14].

However, the Van der Pauw measurements of the type and carrier concentration of the layers grown from the Ga-melt containing 5 wt. % of iron onto Cr-O doped semi-insulating substrates, revealed a surprising fact that these layers are highly *p*-type instead of being highly resistive, as is summarized in Tab. 2.

This fact certainly changes the situation for the explanation of the present S-type instability. The system appears now to possess a similarity to the metal-(thin) SiO_2-*n*-*p* Si device first proposed by Yamamoto and Morimoto[15] in its construction except for the absence of the thin oxide layer and interchange of conduction type in the present case. The latter again exhibists an S-type negative resistance, but its operation principle does not seem to have been well established as yet. In Fig. 8, a more detailed plot of the V-I characteristic of the present device is given, and it can be concluded from this that the actual V-I characteristic of the present device is considerably different in its detail from that of the above mentioned Si-device irrespective of the similarity. The characteristic shown in Fig. 8 is also different from that of any of the double-injection devices mentioned earlier. Obviously, more work is necessary to clarify the mechanism of this new S-type instability and the role played by iron there.

The result of the present doping experiment appears to suggest that iron may act

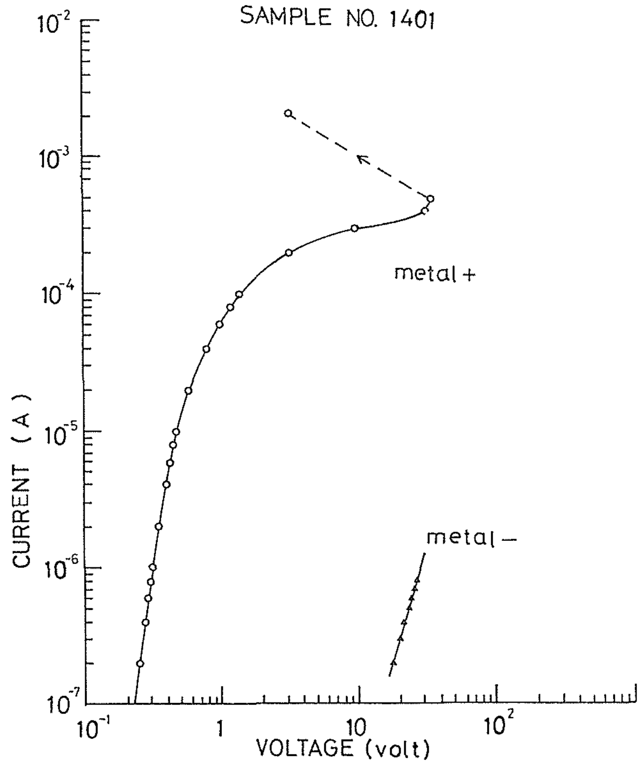

Fig. 8 Logarithmic Plot of V-I Characteristic of Diode with *S*-type Instability

as a shallow acceptor in LPE crystals. Anotner possible interpretation is that the compensation of residual donars by iron atoms acting as deep accepors causes revelation of residual shallow acceptors already present in the epitaxial layer. A simple analysis showed however that the latter explanation does not seem to be able to account for the observed high *p*-type conduction in a quantitative way. On the other hand, the idea of iron atoms acting as shallow acceptors is not in contradiction with the odserved presence of a deep acceptor due to iron in LPE materials[8], because it is probable that iron has two or even more than two possible posible positions to occupy in the GaAs lattice, each of which corresponds to different energy levels. On the basis of such a model, one could speculate that, when the amount of iron in the melt is small, iron atoms preferentially occupy the position for the deep acceptor level on some thermodynamical grounds, but, as the amount of iron is increased, the available number of the position for the deep level, which is again limited thermodynamically, is used up, and then iron atoms start to go into a position for the shallow acceptor level by some complex formation mechanism. The fact that the measured mobility values for holes in the *p*-type layer are extremely small as shown in Tab. 2, suggests the presence of large number of hole traps, and thus, seems to support such a model. It is also possible that, the above speculation, although it requires definitely further experimental support, may also account for the apparently conflicting experimental evidences concerning chromium doped LPE semi-insulating layers mentioned in the introduction.

4. Conclusions

Iron-doped LPE layers were successfully grown from doped gallium melts in a specially developed LPE growth system, which seems to offer several improvements over the previous systems.

The result of the experiment showed a complicated acceptor-like compensation effect by iron, which has not been reported previously. Further work is required to estabish the position of the acceptor levels of iron.

Under certain conditions, the iron doped layers exhibit a new S-type negative resistance effect with related oscillation and switching phenomena. Further work is also required to clarify its mechanism.

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