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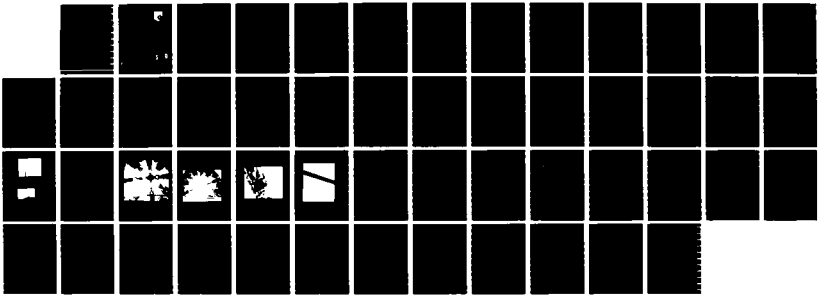

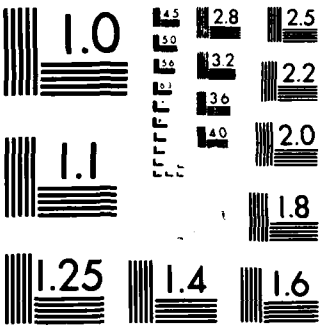

AFWAL-TR-86-1057

GROWTH OF GALLIUM ARSENIDE USING ION CLUSTER BEAM TECHNOLOGY

Robert L. Adams

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August 1986

Final Report for Period 30 September 1983 - 31 May 1984

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The growth of single crystal gallium arsenide (GaAs) epitaxial films on high resistivity GaAs substrates has been demonstrated. Films were grown at substrate temperatures from 600°C down to 400°C with thicknesses from 3000 Å to 5μm. Growth rates were typically 150Å/minute at all growth temperatures with thickness uniformity of ± 5% over the sample (typical sample size 0.7" X 0.7"). The thickness was measured by a standard cleave and stain method. Single crystal behavior was shown using x-ray diffraction and SEM channeling

patterns. Auger analysis was done on the films and showed characteristics comparable to those of the substrate. Hall data taken on the samples found the samples to be n-type, but with very low r bility. The low mobility is the result of defects grown into the structure because of high energy ions impinging on the surface. The energy of the ions was in the range of 100 to 1000 ev because of the small cluster size. The cluster had sizes of 10-50 atoms instead of the desired 500-2000 atoms/cluster. This smaller cluster is likely due to non-uniform heating of the crucibles by the e-beam filament. In addition, the diameter/length of the opening in the nozzle was 1:1. Recent work suggests a 1:10 ratio will allow more interactions and thus enhance the possibility of forming larger clusters. With larger clusters, lower energy per ion will be possible and the native defects will be reduced.

APPENDIX B

U.S. DEPARTMENT OF DEFENSE

SMALL BUSINESS INNOVATION RESEARCH PROGRAM
PHASE I—FY 1983
PROJECT SUMMARY

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Program Office	Proposal No.	Topic No.

TO BE COMPLETED BY PROPOSER

Name and Address of Proposer

Epi-Tech Corporation
5234 East Hatcher
Paradise Valley, AZ 85253

Name and Title of Principal Investigator

Dr. Robert L. Adams, President, Epi-Tech Corporation

Title of Project

Growth of Gallium Arsenide Using Ion Cluster Beam Technology

Technical Abstract (Limit to two hundred words) The growth of single crystal gallium arsenide (GaAs) epitaxial films on high resistivity GaAs substrates has been demonstrated. Films were grown at substrate temperatures from 600° C down to 400° C with thicknesses from 3000 Å to 5μm. Growth rates were typically 150Å/minute at all growth temperatures with thickness uniformity of ± 5% over the sample (typical sample size 0.7" X 0.7"). The thickness was measured by a standard cleave and stain method. Single crystal behavior was shown using x-ray diffraction and SEM channeling patterns. Auger analysis was done on the films and showed characteristics comparable to those of the substrate. Hall data taken on the samples found the samples to be n-type, but with very low mobility. The low mobility is the result of defects grown into the structure because of high energy ions impinging on the surface. The energy of the ions was in the range of 100 to 1000 ev because of the small cluster size. The cluster had sizes of 10 - 50 atoms instead of the desired 500 - 2000 atoms/cluster. This smaller cluster is likely due to non-uniform heating of the crucibles by the e-beam filament. In addition, the diameter/length of the opening in the nozzle was 1:1. Recent work suggests a 1/10 ratio will allow more interactions and thus enhance the possibility of forming larger clusters. With larger clusters, lower energy per ion will be possible and the native defects will be reduced.

Anticipated Benefits/Potential Commercial Applications of the Research or Development The use of this ICB technique will allow deposition of films at temperatures below 600° C for GaAs. At the lower temperatures, the interdiffusion of atoms from the substrate into the epitaxial films should be minimized thereby making sharper interfaces. This deposition technique should lead to the growth of various ternary III/V alloys such as Ga-Al-As in which low temperature growth of high quality films will be critical. Commercial applications of this technique will be for various optoelectronic and microwave device applications.

FOR GOVERNMENT USE ONLY

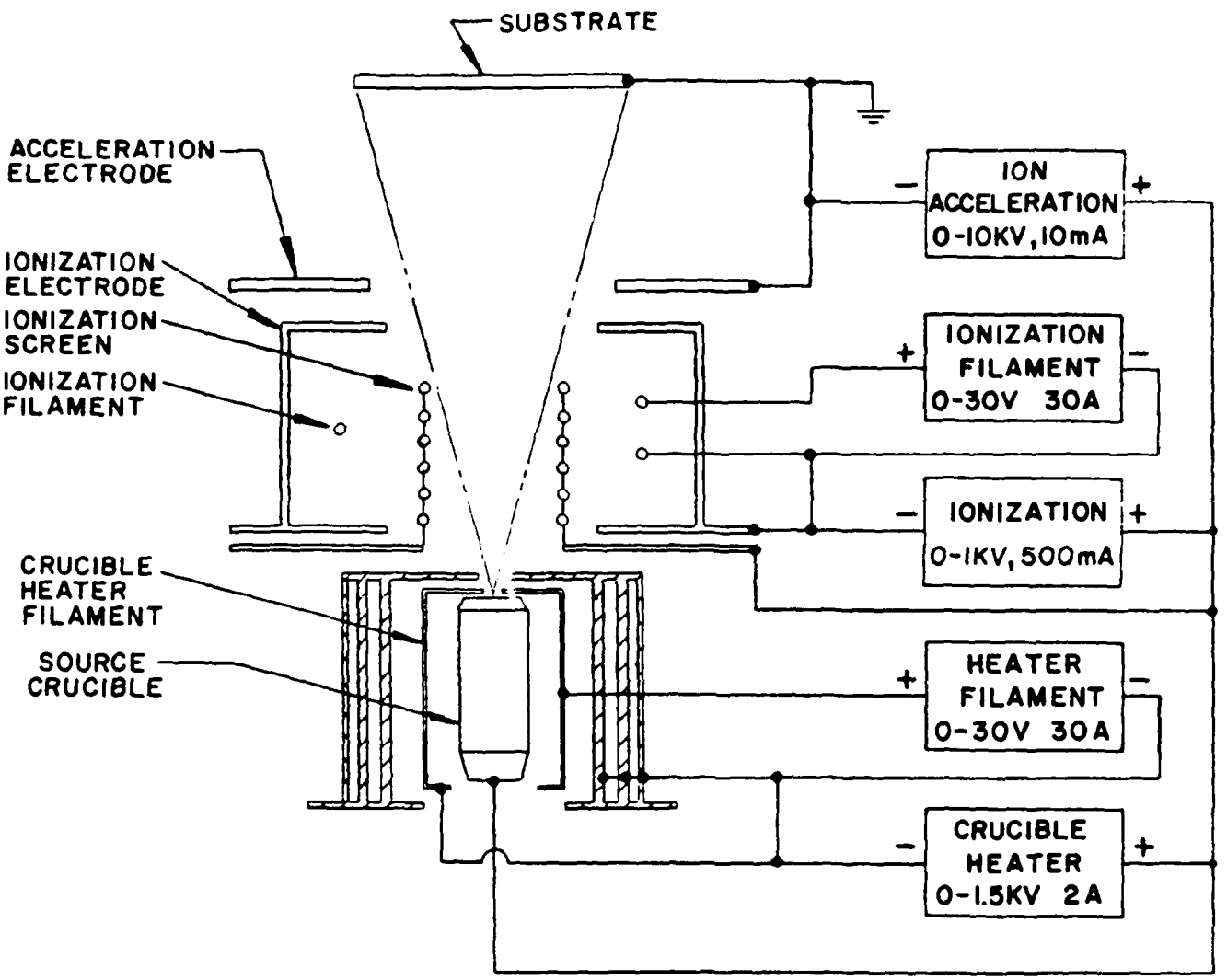
I. Introduction

Contract F33615-83-C-1113 was awarded September 16, 1983, as a Phase I program under the Defense Small Business Innovation Research (SBIR) Program. The program objective was to grow gallium arsenide (GaAs) using Ion Cluster Beam technology. The work was to be done on a newly developed, commercially available ICB machine located in Beverly, Massachusetts, over a period of six months. Samples were then to be characterized using a variety of recognized techniques, and the results were to be compared to other accepted deposition methods.

II. ICB Background

The ICB technology was developed at Kyoto University by Professor Takagi starting in the early 1970's. Initial studies have been directed at the deposition of thin, high quality metal films. The films were of such materials as copper, silver, and gold, and they were of very high quality. The very thin films of gold, 100 Å thick, were "pin hole" free, had electrical resistivities near that of bulk gold, and had densities near theoretical values. Using conventional sputtering, e-beam or CVD techniques, such bulk properties of very thin films have not been obtained.

The standard ICB process can be seen in Figure I. The key to the process is the formation of clusters at the exit port of the crucible. By controlling the temperature of the crucible, the vapor pressure inside the crucible can be regulated to values of approximately 1 torr. With a chamber pressure of 10^{-6} torr, the emerging vapor undergoes a pressure differential of several decades, and interatomic collisions occur in the nozzle area. Under these conditions, rapid vapor expansion followed by super-condensation occurs resulting in the formation of aggregates or clusters. Each cluster contains 500 - 2000 atoms loosely coupled. The escaping clusters can then be ionized by electron bombardment in the ionization section immediately above the crucible. By varying the ionization potential,



ION SOURCE ELECTRICAL SCHEMATIC

Figure 1

the ratio of ionized clusters versus neutral clusters can be changed. In most applications, from 10-30% of the clusters become ionized while the balance are neutral. The ionized clusters can then be accelerated toward the substrate by applying a high negative potential to the accelerating electrodes. While the ionized clusters are accelerated toward the substrate, the neutral clusters continue at ejection velocity. During this transit period, any collision between clusters will cause a break up of the aggregates just as a doubly ionized cluster will also disintegrate.

When the clusters arrive at the surface, the impact causes the cluster to break up with an average kinetic energy of $\bar{E} = QVa/N$ where Q is the electric charge; Va is the acceleration voltage; and N is the number of atoms/cluster. By controlling Va, it is possible to provide each atom in the ionized cluster with enough energy for surface diffusion, ($\bar{E}$ = 1 ev) but less energy than that which will cause surface defects ($\bar{E} > 5$ ev). By controlling electrical charge, which in turn influences film formation, the actual charge content in the total cluster is very low. These features allow the control of energy ranges of 1 - 20 ev per atom. This is in contrast to space charge spreading effects requiring energies to be as high as possible for deposition using charged atomic or molecular ions to ensure proper beam focusing and the maximum intensity. By controlling the energy per atom in the 1 - 20 ev range, the energy necessary for high quality film formation can be supplied without using high substrate temperatures as required in conventional CVD or MBE methods.

In this ICB technique, the ionized clusters are a sig ificant variable to the surface chemistry. The ionized cluster acts as a "surface catalyst" in enhancing surface reactivity and migration.

The system used to grow GaAs has two cluster sources following the same principles discussed above. On the specific machine employed for deposition, each source had an independent heating and ionization section, but a common acceleration electrode. This meant that clusters from both Ga and As had the

same acceleration potential and not independent supplies. This limitation does not present a severe problem in current studies and is solvable with existing hardware.

III. ICB Deposition Equipment and Procedures

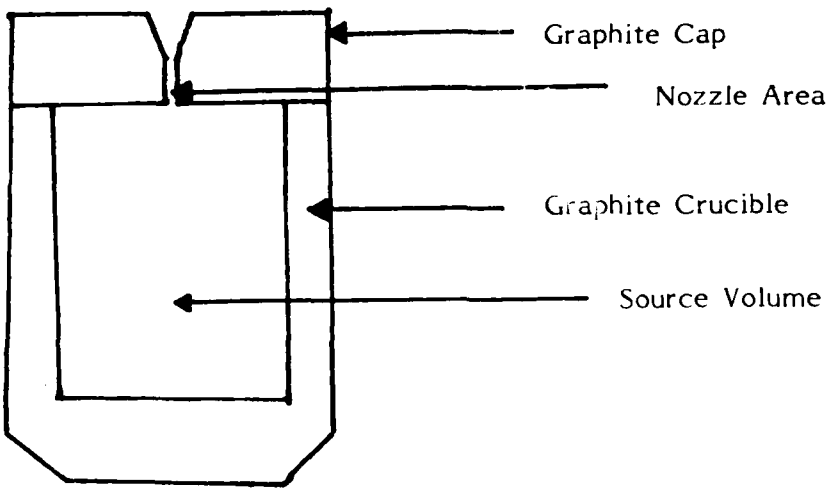
The ICB system use has been developed by Eaton Corporation through collaborative efforts with Profess Takagi of Kyoto University. The Eaton ICB system used in this work is a mul ource machine using e-beams to heat each high purity graphite crucible. The graphite crucibles are shown in Figure 2. The gallium crucible contained 15 rams of charge material and the other crucible held from 5 - 7 grams of arsenic.

The acceleration ele trodes provide potential from 0 - 5 Kev on all sources simultaneously. Becau e of problems in the power supplies, the present machine does not allow each sour to be accelerated independently. Although the acceleration is a common valu , the amoun of ionization applied to each source as well as the power to the e-beam heater can be regulated separately. The sample area available for deposition is 10 cm X 10 cm.

The substrate is heated by infrared lamps immediately above the sample and controlled by a thermocouple feed-back system. The substrate temperature can be varied from room temperature to 800° C and controlled very accurately by the Barber- Colman unit.

The sources are in a Balzers vacuum chamber with a large diffusion pump providing the system vacuum. The standard operating levels are 1 - 10 X 10^{-7} torr with no sample ionization and 1 x 10^{-6} torr with material deposition. On several occasions, the chamber door was opened to add arsenic after allowing sufficient time for cooling of the gallium source. Following recharge of the arsenic, the chamber was closed, and the pumping restarted. The typical cycle time from initial cool-down until resumption of growth was 2 - 3 hours. When growth was resumed, morphology, growth rates, and uniformity in thickness reproduced extremely well. Samples were loaded into the chamber through a turbo-

Crucible Used in January



Crucible Used in March

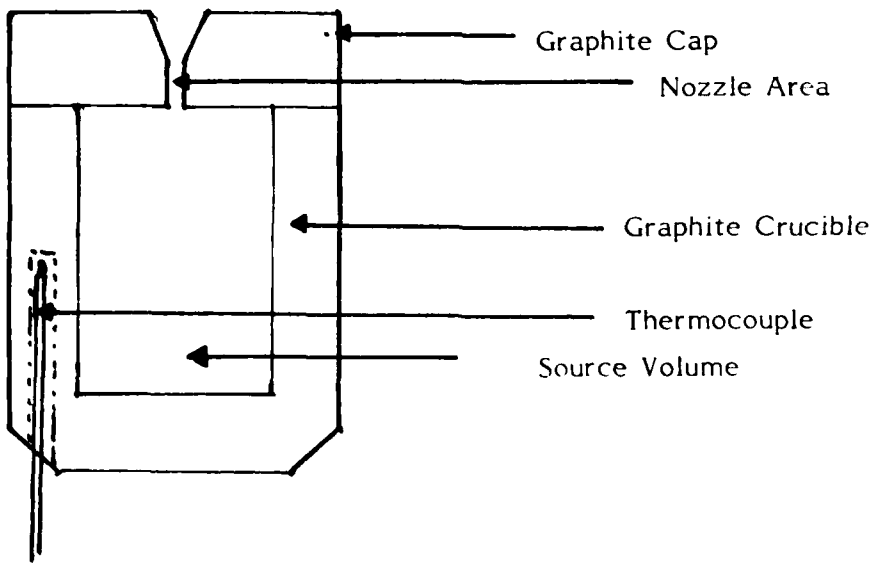


Figure 2

pumped load lock by means of a walking beam meachanism Total time for either loading or unloading was approximately 2 minutes. The deposition rate and thickness were monitored by a quartz crystal near the substrate using the appropriate calibration and tooling factors for the specific set-up and material. Although a Fluke controller is included on the system using a single crucible source, the multi-source system was operated purely in a manual mode.

The run procedure developed for the GaAs was different than that used for other ICB depositions on the same equipment because of the volatility of the arsenic from the wafer surface. In the first set of experiments conducted in January, the wafers were etched in a $H_2SO_4O_2$:H_2O (5:1:1) solution, rinsed in deionized water and blown dry with filtered nitrogen. The samples were then placed on a carrier shown in Figure 3. Each of the two samples was 0.7" X 0.7" on edge and .014" thick.

Prior to loading each sample into the growth chamber, the gallium source was heated to 1225° C, and the deposition rate was established by using the Inficon quartz crystal monitor system. After this was completed, the gallium beam was blocked by a manually operated shutter, and the arsenic source was then heated. Because of the low sublimation temperature of arsenic, only the heating elements of the e-beam heater were used without any electron bombardment to establish the deposition conditions. Because arsenic will not stick to the crystal monitor, the arsenic flux was monitored by watching the system pressure. This is a very difficult way to control the arsenic, since a change of 1° C can alter the vapor pressure a significant amount.

For some of the initial work, a thermocouple was placed in the side of the crucibles, and the temperatures read directly. This proved to be a problem, however, because the thermocouple was not floating at the same 10 Kev as the crucible, and thus caused arcing problems. Therefore, some runs, as noted on the data sheet, will show crucible temperature, but the majority will not.

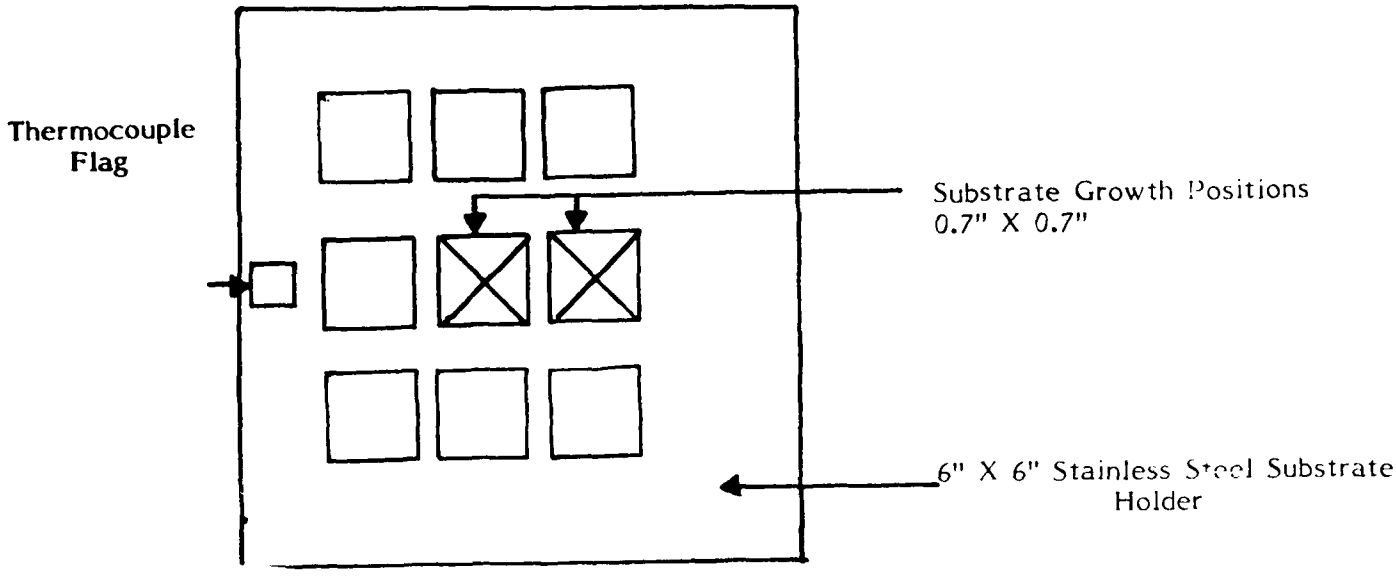


Figure 3

Note: Drawings not to Scale

Throughout a run, the operator was always trying to adjust the power supply to keep the pressure at a constant value. Once the arsenic was stabilized, the sample was moved into the growth chamber, the heating lamps turned on, and the shutter over the arsenic source opened to allow surface bombardment by the arsenic to prevent surface erosion by arsenic evaporation. Once the sample was at temperature, the gallium shutter was opened, and growth initiated.

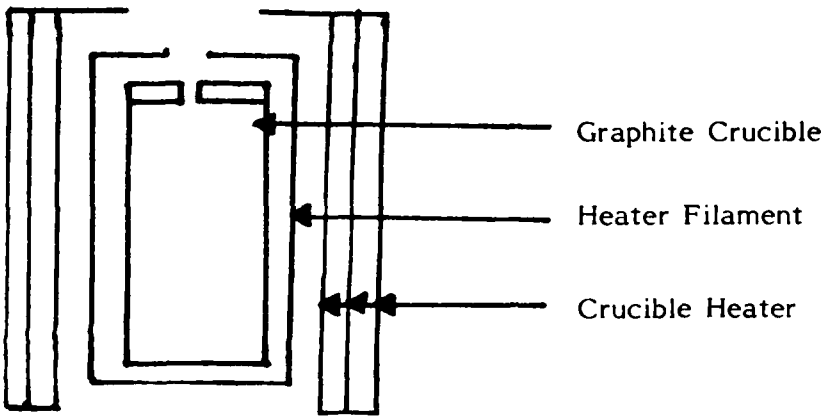
The ionization section on each source as well as the acceleration potential for some samples had been set prior to commencing growth. Although the machine is designed to have 10 Kev of acceleration, the presence of the arsenic vapor in the acceleration and ionization section causes arcing to occur, and thus limits the acceleration to 5 Kev. As stated earlier, the acceleration section was common for both the Ga and As source, so independent measurements could not be made. After growing the desired time, the gallium shutter was closed, and the heat was turned off. When the sample was below 400° C, it was moved into the load lock and then into the atmosphere, and the cycle was repeated.

As the samples were evaluated following the first series of experiments, the sample thicknesses were very thin, i.e. 100 - 500 Å. The discussion of these samples can be found in the results section.

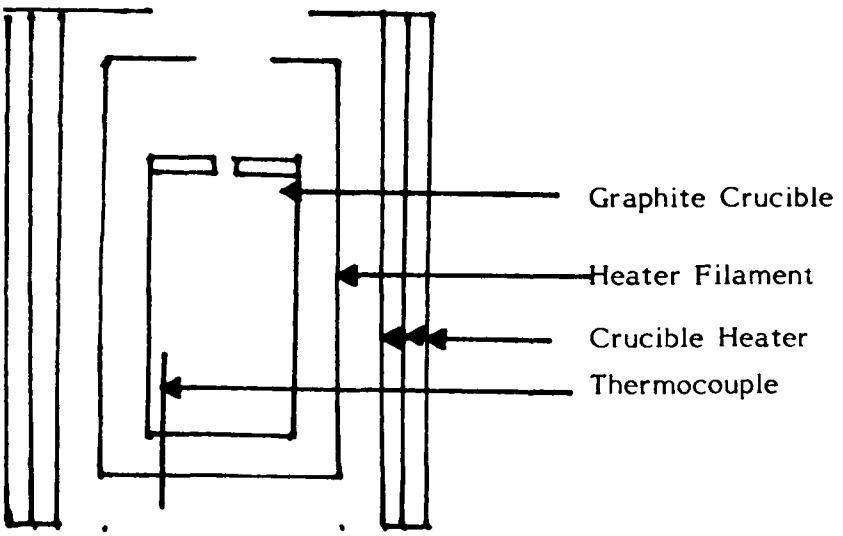
The lack of growth precipitated some procedure and hardware changes for the second set of experiments done in March. For the hardware, the change involved the redesign of the heater around the gallium crucible so that more power could be applied to the top of the crucible. In this manner, the "spitting" seen in the first set of runs with 6% power was absent in the second set at 16 %. As can be seen in Figure 4, the longer heater kept the nozzle area hotter, thus reducing condensation in this area.

Three significant changes were made in the deposition procedures for the second set of runs. The first involved the control of the arsenic pressure. The RGA was used to monitor the arsenic pressure with manual controls still

Original Configuration



Modified Configuration
Lengthened Heater and Thermocouple



Note: Figure is not to Scale

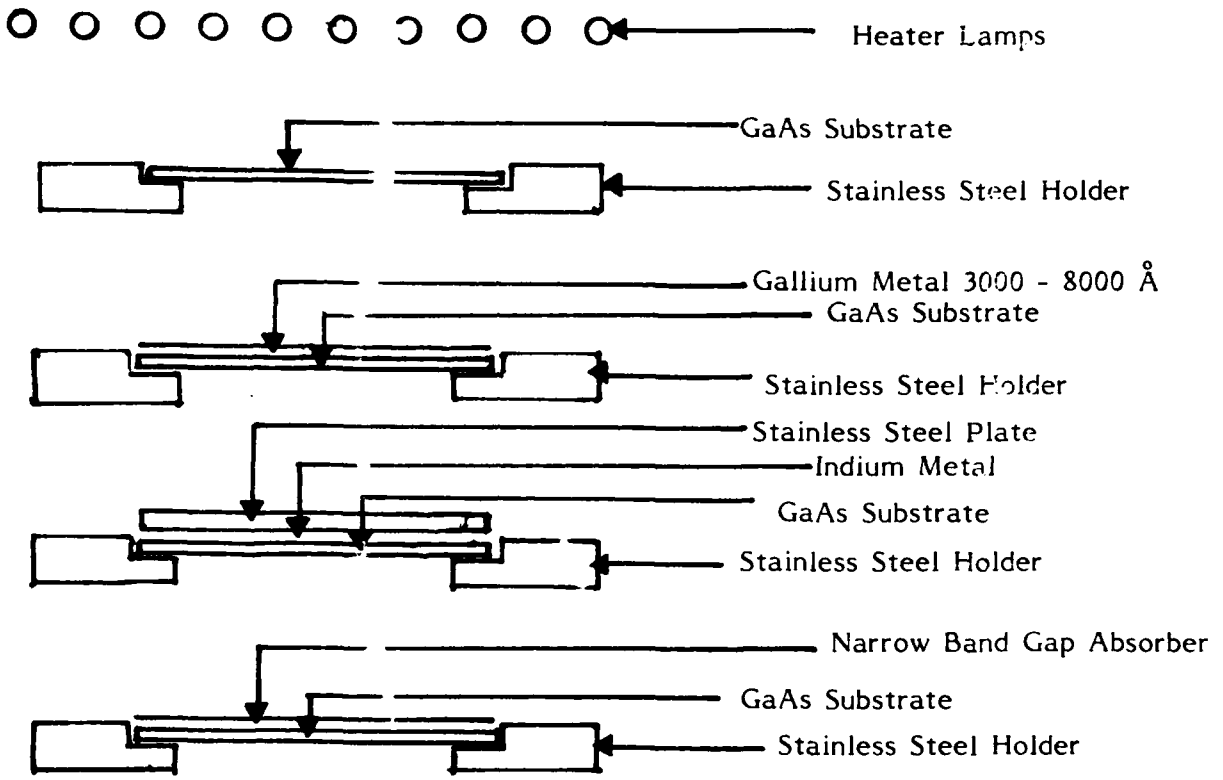
Figure 4

being used to adjust the temperature to compensate for changes. This procedure was more sensitive in controlling the arsenic pressure than the chamber pressure gauge.

The second change involved wafer clean-up. After struggling with inadequate wafer clean-up stations, it was decided to grow on the substrates with no initial clean-up either by solvent or acid treatment. The surfaces of the grown wafers were excellent as can be seen in the results section of this report. This ability to grow on substrates with no clean up prior to deposition is truly unique to this deposition technique, and is discussed further in the results section.

The third significant change involved the heating of the substrate. In the first set of experiments, the lack of substantial growth could have been attributed to the very low substrate temperatures. The low temperatures were due to the infrared light transmission characteristics through the GaAs as opposed to the absorption of infrared by metals or other semiconductors such as silicon. In order to get better absorption, three different approaches were tried. In one approach, a piece of stainless steel was placed over the sample with no bonding material. A second approach had various thicknesses of gallium deposited on the back of the wafers. The third approach had a thermal bonding agent, either gallium or indium, on the back of the wafer holding it to the stainless steel back plate. This latter approach was most successful, although it required the most time for preparation and de-mounting. A schematic can be seen for the three methods in Figure 5.

Using the modified hardware and process parameters, films were successfully grown using the ICB equipment. However, the equipment had several problems that will need to be corrected for future work with GaAs. The heaters for both Ga and As need to be altered so that very precise temperature control can be maintained on both sources. Each source must also be uniformly heated.



Cross Section of Different Wafer Mounting Schemes and Substrate Holder

Note: Drawings not to Scale

Figure 5

The most likely solution will be a heating lamp method currently being evaluated.

A second major problem involves the power supplied in the system. Because the sample is at 0 potential, all the power supplies operate on top of a 10 Kev potential which causes many problems. As a result of these conditions, modified power supply designs are being studied and will be implemented. Also, a machine to do GaAs will need a RGA that will go to 300 a.m.u. and a quad head that can be used for some flux measurements in the deposition area. Such hardware modifications and additions are now being evaluated and will be included on the next GaAs system. By making these and other small changes, the redesigned hardware should support the process for growth of GaAs in a more controlled and reproducible manner.

IV. Summary of Epitaxial Run Conditions

The run conditions will be divided into two groups. Table I will represent the work done in the January experiments, and Table II will represent the results from the March work.

As can be seen in both tables, pieces of data on specific run conditions are omitted. In most cases such as the temperature readings for the Ga and As crucible, no read-outs were available in January. In March, the high voltage in the system interacted with the thermocouple on many occasions, causing arcing or blowing power supplies. As discussed in an earlier section, the heater filament of the arsenic crucible was never turned on because of the low temperature requirements for arsenic. In Table I thickness measurements are not stated for all samples because of the very thin layers. The cleaning process and mounting procedures made it impossible to use a surface profileometer such as a Dek-Tak to measure a step and the standard stain and cleave procedures will not resolve layers <3000 Å. The deposition rate numbers were found to be very erratic throughout the program, thereby making these values suspect. In some of the last runs,

EXPLANATION OF PARAMETERS

Substrate		This indicates the coping of the GaAs - Si = silicon U = undoped Cr = chromium
Crucible I Ga	FV (V)	Forward voltage in Volts of filament on Ga crucible
	FI (A)	Forward Current amps of filament on Ga crucible
	SV (V)	e-beam supply vol e in amps on Ga crucible
	SI (MA)	e-beam supply curr in amps on Ga crucible
Ionization I Ga	FV (V)	Forward voltage in ts of Ionization section above Ga crucible
	FI (A)	Forward Current ir mps of Ionization section above Ga crucible
	SV (V)	Supply Voltage of I eam source in Ionization section above Ga crucible
	SI (MA)	Supply current of I am source in Ionization section above Ga crucible
	Accel Kev	Acceleration poten on Ga beam in Kev
Crucible II As	FV (V)	Forward voltage in ts of filament on As source
	FI (A)	Forward current in ps of filament on As source
	SV (V)	E-beam supply voltag in volts of filament on As source
	SI (MA)	E-beam supply current n Ma of filament on As source
Ionization II As	FV (A)	Forward voltage in volts of Ionization section above As crucible
	FI (V)	Forward current in Ma of Ionization section above As crucible
	SV (A)	Supply voltage of E-beam source in Ionization section above As crucible
	SI (MA)	Supply current of E-beam source in Ionization section above As crucible
	Accel Kev	Acceleration potential on As beam in Kev
Press.		Pressure in chamber in Pascal
Ga Cruc. temp.		Temperature of Ga crucible
As Cruc. temp.		Temperature of As crucible
Sub. temp.		Indicated temperature of substrate by thermocouple monitor
Dep'n. Rate		Deposition rate as read on crystal monitor - Angstroms/sec.
PWR		Power on Ga crucible as a % of total available power
Thickness		Thickness of epi layer grown

TABLE I

Run #		1	2	3	4	5	6	7	8	9	10	11	12
Substrate		Si	Si	Si	Si	Si	Si	Cr	Cr	Cr	Cr	Cr	Cr
Ga Crucible	FV	42	41.6	42.2	42.1	41.9	42.8	41.5	Ran out of As before run conditions were established and recorded	40.2	40.4	40.9	39.7
	FI	17.1	17.0	17.0	17.1	17.2	17.0	17.0		16.7	16.8	16.9	16.7
	SV	360	360	360	350	400	400	350		360	350	340	380
	SI	520	530	540	540	460	580	460		430	460	470	410
Ga Ionization	FV	43.9	12.2	11.0	11.3	11.5	11.0	12.3		12.4	12.2	12.1	12.2
	FI	17.3	11.1	10.5	10.7	10.7	10.4	11.2		11.2	11.2	11.2	11.2
	SV	---	300	100	100	100	110	300		300	290	300	300
	SI	---	337	113	133	128	92	315		308	335	285	269
Ga Accel.		0	0	1	2	4.1	4	3		3	4	5	3
As Crucible	FV	5.7	5.4	5.0	5.0	5.9	5.7	5.8		5.9	5.0	5.3	5.3
	FI	5.3	4.8	4.7	4.7	4.9	4.7	4.7		5.1	4.5	4.6	4.6
	SV	---	---	---	---	---	---	---		---	---	---	---
	SI	---	---	---	---	---	---	---		---	---	---	---
As Ionization	FV	---	13.2	11.9	12.6	---	13.5	13.7		13.2	13.5	13.6	13.7
	FI	---	11.4	10.9	11.4	---	12.3	12.4		12.0	12.2	12.4	12.4
	SV	---	300	110	110	---	100	310		300	310	310	310
	SI	---	211	---	158	---	253	305		288	332	276	285
As Accel.		0	0	1	1	4	4	3		---	4	---	3
Pressure		$3X10^{-4}$	$5X10^{-4}$	$3X10^{-4}$	$5X10^{-4}$	$3X10^{-4}$	$4.5X10^{-4}$	$7X10^{-4}$		$6X10^{-4}$	$5X10^{-4}$	?	$5X10^{-4}$
Ga Cruc. temp.		---	---	---	---	---	---	---		---	---	---	---
As Cruc. temp		---	---	365	365	---	---	---		---	---	---	---
Sub Temp.		601	600	600	600	600	600	600		600	550	500	600
Dep'n. Rate		3.4	---	---	---	2.5	3.2	3		4.2	4.6	5.8	3.9
Power (%)		7	7	7	7	7	7	6		7	7	6	6
Thickness		0	0	0	?	<3000	<3000	<3000		<5000	?	?	?

TABLE II

Run #	1	2	3	4	5	6	7	8	9	10	11	12
Substrate		Cr	Cr	Cr	U	U		U	U	U	U	
Ga Crucible FV		30.0	30.3	30.3	30.2	30.2		29.9	29.6	29.7	31.2	
Ga Crucible FI		16.3	16.3	16.3	16.4	16.4		16.0	16.2	16.3	16.8	
Ga Crucible SV		790	700	690	780	780		670	860	890	780	
Ga Crucible SI		520	690	660	590	590		690	560	520	590	
Ga Ionization FV		12.7	12.7	12.5	13.1	13.1		12.4	12.4	12.5	12.7	
Ga Ionization FI		11.6	11.6	11.6	11.8	11.8		11.4	11.4	11.5	11.6	
Ga Ionization SV		300	310	320	290	290		300	300	300	300	
Ga Ionization SI		299	324	267	340	340		285	278	269	275	
Ga Accel.		3.0	3.0	3.0	3.0	3.0		3.0	3.0	3.0	3.1	
As Crucible FV		6.1	5.7	5.9	4.8	4.8		6.0	5.0	5.2	4.9	
As Crucible FI		5.1	5.0	5.0	5.3	5.3		6.0	5.4	5.5	5.3	
As Crucible SV		---	---	---	---	---		---	---	---	---	
As Crucible SI		---	---	---	---	---		---	---	---	---	
As Ionization FV		12.3	---	---	11.5	11.5		12.1	12.1	12.1	12.6	
As Ionization FI		10.6	---	---	9.8	9.8		10.2	10.3	10.3	10.4	
As Ionization SV		---	---	---	300	300		300	300	300	300	
As Ionization SI		---	---	---	011	011		11	12	15	13	
As Accel.		---	---	---	---	---		---	---	---	---	
Pressure		$8X10^{-4}$	$8X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$		$4X10^{-5}$	$8X10^{-4}$	$8X10^{-4}$	$10X10^{-4}$	
Ga Cruc. temp.		---	1225	1225	1205	1205		---	1220	1220	---	
As Cruc. temp		368	---	371	325	325		340	344	353		
Sub Temp.		600	600	600	600	600		600	600	600		
Dep'n. Rate		6.0	6.5	5.5	---	---		---	---	---		
Power (%)		16	16	16	16	16		16	17	17	16	
Thickness		3500	?	?	2100	3000		2800	4000	14000	?	

Ga deposition backs of wafers only. No As. Done to check absorption properties.

Run aborted -- Mechanical problem loading sample into chamber

Run #		13	14	15	16	17	18	19	20	21	22	23	24
Substrate		U	U	U	U	U	U	U	U	U	U	U	U
Ga Crucible	FV	31.4	30.6	30.6	30.6	33.0	30.4	31.0	31.7	31.1	30.5	30.3	31.4
	FI	16.8	16.6	16.6	16.6	18.1	16.3	10.5	16.7	16.6	16.4	16.3	16.4
	SV	730	730	730	730	720	730	720	710	720	700	730	560
	SI	650	630	630	630	450	650	780	640	620	700	620	830
Ga Ionization	FV	12.5	12.6	12.6	12.6	10.9	---	12.7	12.6	13.0	13.0	12.6	12.7
	FI	11.5	11.6	11.6	11.6	10.5	---	11.6	11.6	11.7	11.7	11.6	11.6
	SV	310	310	310	310	290	---	300	310	300	300	310	300
	SI	301	310	310	310	278	---	235	?	300	300	300	291
Ga Accel.		3.0	3.0	3.0	4.0	---	---	3.0	3.0	1.0	2.0	4.6	0
As Crucible	FV	5.2	4.0	4.0	4.0	6.6	6.6	6.5	5.4	5.9	6.4	5.9	6.2
	FI	6.6	5.1	5.1	5.1	5.3	5.4	5.0	5.5	4.6	4.8	4.5	4.6
	SV	---	---	---	---	---	---	---	---	---	---	---	---
	SI	---	---	---	---	---	---	---	---	---	---	---	---
As Ionization	FV	12.0	12.4	12.4	12.4	10.9	---	12.2	12.1	12.2	12.1	12.0	12.1
	FI	10.3	10.5	10.5	10.5	9.6	---	10.4	10.2	10.2	10.2	10.2	10.3
	SV	310	290	290	290	290	---	300	300	300	300	310	310
	SI	13	20	20	20	14	---	11	11	11	11	12	15
As Accel.		3.0	3.0	3.0	4.0	0	---	3.0	3.0	1.0	2.0	4.6	0
Pressure		$9X10^{-4}$	$9X10^{-4}$	$9X10^{-4}$	$9X10^{-4}$	$9X10^{-4}$	$9X10^{-4}$	$9X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$
Ga Cruc. temp.		1210	1210	1216	1216	---	---	---	1220	1220	1220	1220	---
As Cruc. temp		---	---	---	---	---	---	---	---	---	---	---	---
Sub Temp.		500	400	300	400	400	400	400	500	400	400	400	300
Dep'n. Rate		---	---	--	---	---	---	---	---	5.0	4.5	2.4	2.4
Power (%)		16	16	16	16	16	16	16	16	16	16	16	16
Thickness		10,000	---	10,000	5,000	6,000	0	20,000	50,000	10,000	8,500	9,000	8,500

Run #		25	26	27	28	29	30	31	32	33	34	35		
Substrate		U	U	U	U	U	U	U	U	U	U	U		
Ga Crucible	FV	31.7	32.1	31.2	31.3	30.9	31.4	29.2	32	32	31	31		
	FI	16.6	16.8	16.5	16.4	11.5	16.6	15.8	16	16	16	16		
	SV	550	670	610	600	650	560	810	650	470	560	550		
	SI	900	720	780	810	720	830	550	750	990	850	800		
Ga Ionization	FV	12.7	12.9	13.0	12.7	12.6	12.7	12.6	13.0	13.0	9.9	9.6		
	FI	11.5	11.7	11.7	11.6	11.6	11.6	11.5	11.0	11.8	9.8	9.9		
	SV	310	310	300	300	300	310	310	300	300	310	320		
	SI	300	300	300	300	300	310	309	300	389	7	10		
Ga Accel.		1	2	4	3	4.8	3.0	2.7	3.0	2.5	3.0	3.0		
As Crucible	FV	6.9	6.5	6.0	5.8	6.0	5.8	6.4	7.3	9.1	7.2	7.3		
	FI	5.0	4.9	4.4	4.5	4.6	4.5	5.0	5.1	6.1	6.4	6.4		
	SV	---	---	---	---	---	---	---	---	---	---	---		
	SI	---	---	---	---	---	---	---	---	---	---	---		
As Ionization	FV	11.8	12.7	12.2	12.2	12.4	12.2	11.9	?	?	12.3	12.9		
	FI	10.1	10.3	10.1	10.2	10.3	10.2	10.0	?	?	10.3	10.7		
	SV	310	300	300	300	300	300	300	?	?	300	290		
	SI	10	11	10	11	11	11	9	?	?	14	32		
As Accel.		1	2	4	3	4.8	3	2,7	3	?	3	3		
Pressure		$8X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$	$7X10^{-4}$	$6X10^{-4}$	$7X10^{-4}$	$6X10^{-4}$	$9X10^{-4}$	$1X10^{-3}$	$1X10^{-3}$	$1X10^{-3}$		
Ga Cruc. temp.		---	1225	1225	1225	1225	1207	1165	---	---	1230	1225		
As Cruc. temp		---	---	---	---	---	---	---	---	---	---	---		
Sub Temp.		300	300	300	400	400	500	500	400	400	400	400		
Dep'n. Rate		2.4	1.7	2.2	---	---	2.2	5.5	---	---	---	---		
Power	(%)	16	16	16	16	16	16	16	16	16	16	16		
Thickness		5000	12,500	10,000	5,000	12,500	21,300	?	7,000	?	?	?		

correction factors were included to help modify the numbers and to correlate with the values measured by Dek-Tak. When the corrections were made, deposition rates of 2.4 - 2.6 Å/sec. were observed, iving rowth rates of 120 - 150 Å/min. The geometry of the system will make the crystal monitor very inaccurate until modifications are made. Also, the acceleration values for Ga and As are not always recorded as being equal. In reality, they are equal because of the hardware wiring. The discrepancy is merely from the set point of the arsenic not being adjusted to read the same as the Ga.

A portion of the conclusion will address the changes required to allow the ICB equipment to deposit GaAs. Also, fundamental discussions as to the equipment design as it relates to the process physics will be covered at length.

V. Experimental Results

In the proposal submitted and awarded, the anticipated results were:

a. Growth of single crystal GaAs on GaAs substrates starting with Ga and arsine.

b. Parameters for growth of GaAs epi on GaAs substrates at temperatures below 600° C.

c. Characterization of the films as to their electrical and physical properties.

Of these anticipated objectives, only one was modified. A single source machine had been expected at the time the proposal was written, and it would have necessitated the use of Ga and AsH_3 as the starting materials. The availability of the multi-source machine in time for the work made this approach unnecessary. With the exception of this one change, all the objectives of the proposal were met.

Single crystal GaAs epi was grown on GaAs substrates. Single crystal epi was grown at temperatures below 600° C. Samples were characterized as to their electrical, chemical, and physical properties. This section will discuss in detail the experimental methods used and the results obtained by each technique

for the samples grown.

A. Film Thickness Uniformity and Morphology

The thickness of the films was measured by two techniques; surface profiling and cleaved cross sections. The surface profiling was done using a Dek-Tak system sold by Sloan Instruments. In this simple test, a step height was measured from the grown film to the starting substrate. As can be seen in Figure 3, the holder provides a "masked" area for the substrate. This method worked exceedingly well in the March work where samples were not etched in the H_2SO_4:H_2O_2:H_2O (5:1:1) mixture prior to deposition. This etch "rounded" the surfaces at the wafer edges and made the Dek-Tak ineffective. With the second set, well defined traces were obtained as shown in Figure 6 with clearly defined steps of 4000 Å and less.

The second technique used was the conventional cleave and stain technique. A selective etch, CrO_3:HF:$AgNO_3$:H_2O, was used to delineate the film/substrate interface. Using a high power optical microscope equipped with differential interference contrast (DIC), the thickness could easily be read. This technique, however, is limited to films with thicknesses of > 3000 Å. Using this technique, the substrate/epi interface can be evaluated for smoothness. A given sample was cleaved into four pieces, and the thickness was measured at 12 points across the sample. The values were all within ± 10% at each location. This ± 10% is the experimental error of the technique. On the sample measured, the thickness was 1.0 ± 0.1μm for the 0.7" X 0.7" sample. The Dek-Tak value was 9000 Å for the same sample. Three two-inch diameter samples were also grown, but the best sample was used for electrical data, and the other two samples had mechanical problems that caused non-uniform thicknesses. In one sample, a shutter partially shielded the sample, and in the second, the arsenic was depleted, and the run continued longer than it should have. On the only good sample, the perimeter values appeared very uniform around the wafer as determined by the Dek-Tak,

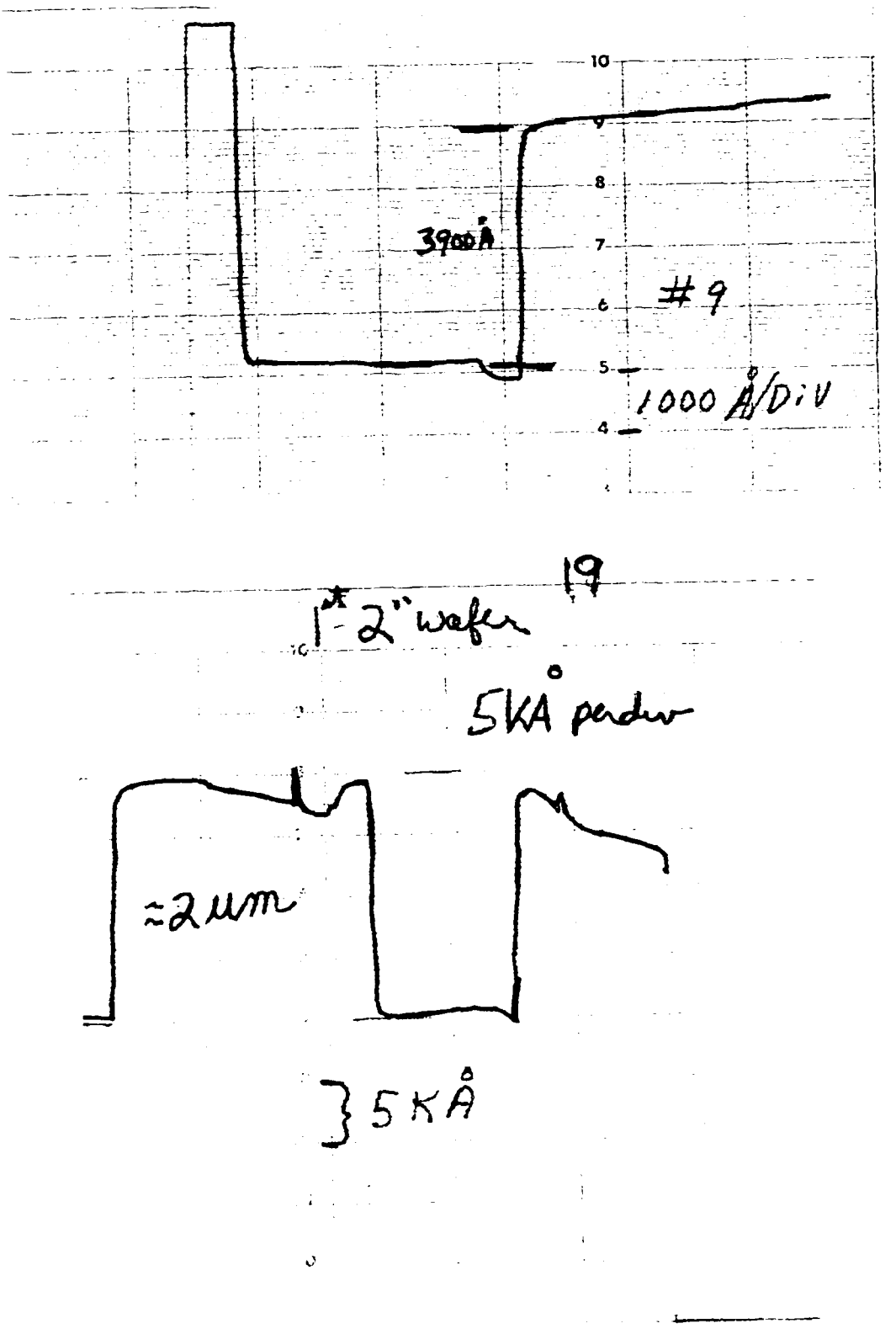


Figure 3

but the center values were not measured by the cleave and stain method. The uniformity was checked on a second sample and was found to have the same range of values, i.e. ± 10%.

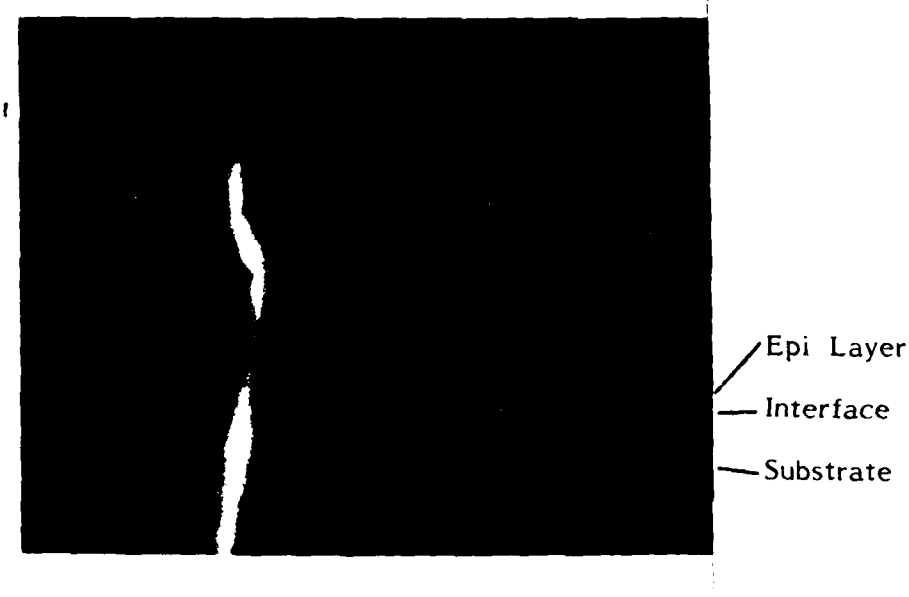
On all samples evaluated by the cleave and stain method using DIC, the interface was very smooth and straight as seen in Figure 7. The smooth interface on the samples which had not previously been cleaned, is indicative of a unique process. uch interfaces on either a VPE or MBE sample with no cleaning would not have the same high quality.

Further evidence of the unique film deposition parameters is the surface morphology. As can be seen in the micrograph of the surface in Figure 8, the surface of both the substrate and epitaxial film are identical. This epitaxial film is 1.0μm thick and appears the same as the uncleaned substrate area when both are examined at 200X using DIC. This featureless surface was typical of all surfaces until the thicker samples were evaluated. The surface roughness seen on the thicker samples can be attributed to the mismatch in the cell parameters measured in the epitaxial film and substrate. This information will be discussed in the next section.

With the techniques used for this section of evaluation, the ICB method produces uniform film thickness and very smooth surfaces. Also, this method has a unique property of cleaning the interfaces prior to deposition in order to produce a surface that is atomically clean.

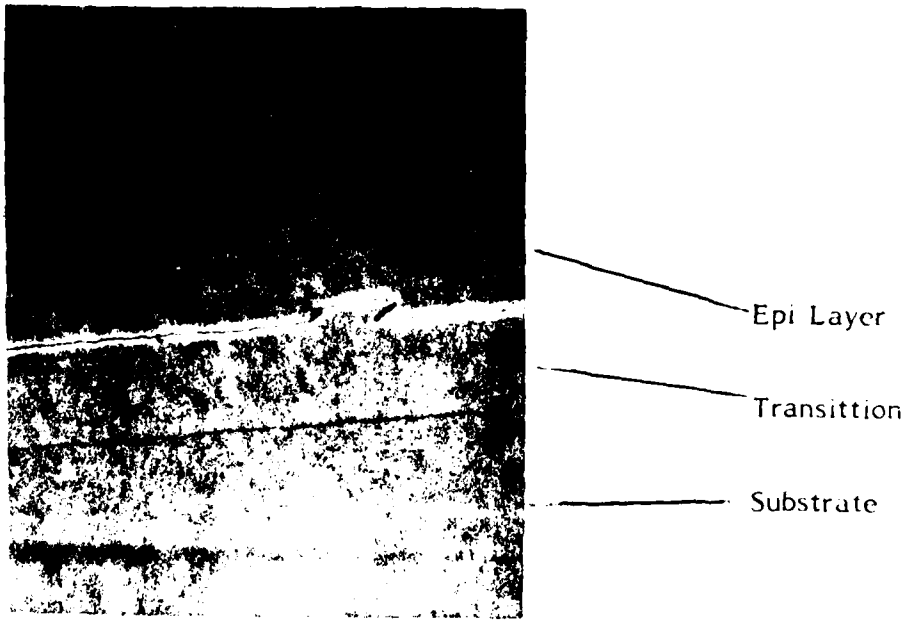
B. Structural Properties

The structural properties of the samples were measured in two ways; x-ray diffraction and SEM channeling. The reason for the exhaustive structural analysis was to determine if the films were single crystal. Some of the electrical data measured were abnormal, thereby suggesting the possibility of amorphous or polycrystalline films. The first study was done with a scanning electron microscope (SEM). Using the SEM, electron channeling patterns are generated as a



Cleaved and Stained Cross Section
(Magnification = 1000 X)

Figure 7



Surface Topography
(Magnification = 100 X)

Figure 8

result of the crystallographically dependent electron backscattering from the surface regions of crystalline material. The scattering of a 30 Kev beam is primarily from the 500 - 1000 Å region. Using this method, the crystalline properties can be evaluated across a given sample by measuring the channeling patterns generated and comparing them. The whole of each surface examined gave the same 100 patterns as shown in Figure 9. At even lower energies, 5Kev, 100 patterns were also obtained for the surface images.

To examine the problem further, a sample was cleaved, and the 110 planes were evaluated. The patterns obtained were 110 at the surface, proving the single crystal nature of the film as shown in Figures 10 and 11.

One interesting aspect of this evaluation was the cross section shown in Figure 12. The epi layer is much brighter than the substrate. This is due, possibly, to a difference in electrical conductivity. Since the SEM electrons are being introduced into the lattice by ionization, the illumination could be from reradiation of the secondary electrons from native defects in the films. The x-ray diffraction technique was used as a cross check to measure the single crystal nature of the film. Also, the x-ray diffraction work can be used to determine unit cell parameters using the low incident angle technique. In the two x-ray traces seen in Figures 13 and 14, the two effects can be seen. On sample #20, the presence of the second peak on the 422 reflection is evidence of different cell sizes with the surface having a cell value of 0.1% less than the substrate. By contrast, sample #33 shows a well resolved 422 reflection with 109 seconds as the width at 1/2 max and an intensity ratio of 218/14 = 15 in arbitrary units. This ratio combined with the narrow reflection indicates a well defined single crystal with lattice parameters matching the substrate. Sample #33 had arsenic pressures of 13×10^{-4} Pascal as opposed to 8×10^{-4} Pascal for #20. The presence of the extra arsenic allowed the formation of the correct cell size. Other scans of the 511 and 422 peak show the films to be single crystal.

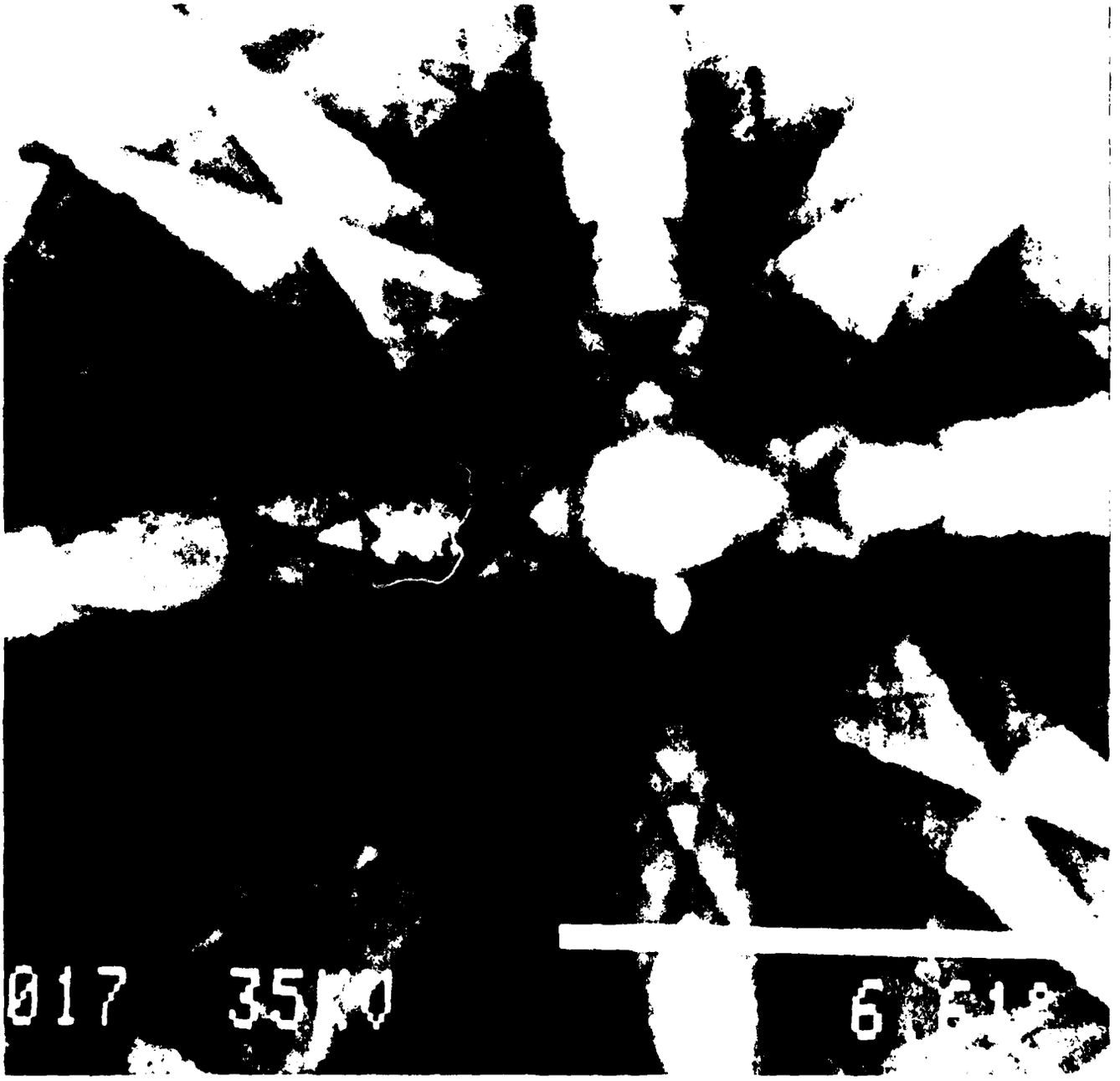


FIGURE 9

ELECTRON CHANNELING PATTERN OBTAINED FROM SAMPLE 4A
ELECTRON BEAM ENERGY 35 keV.

The clarity of the pattern and the presence of high order lines indicates the perfection of the crystal surface region. The pattern can be indexed as a {100} orientation.

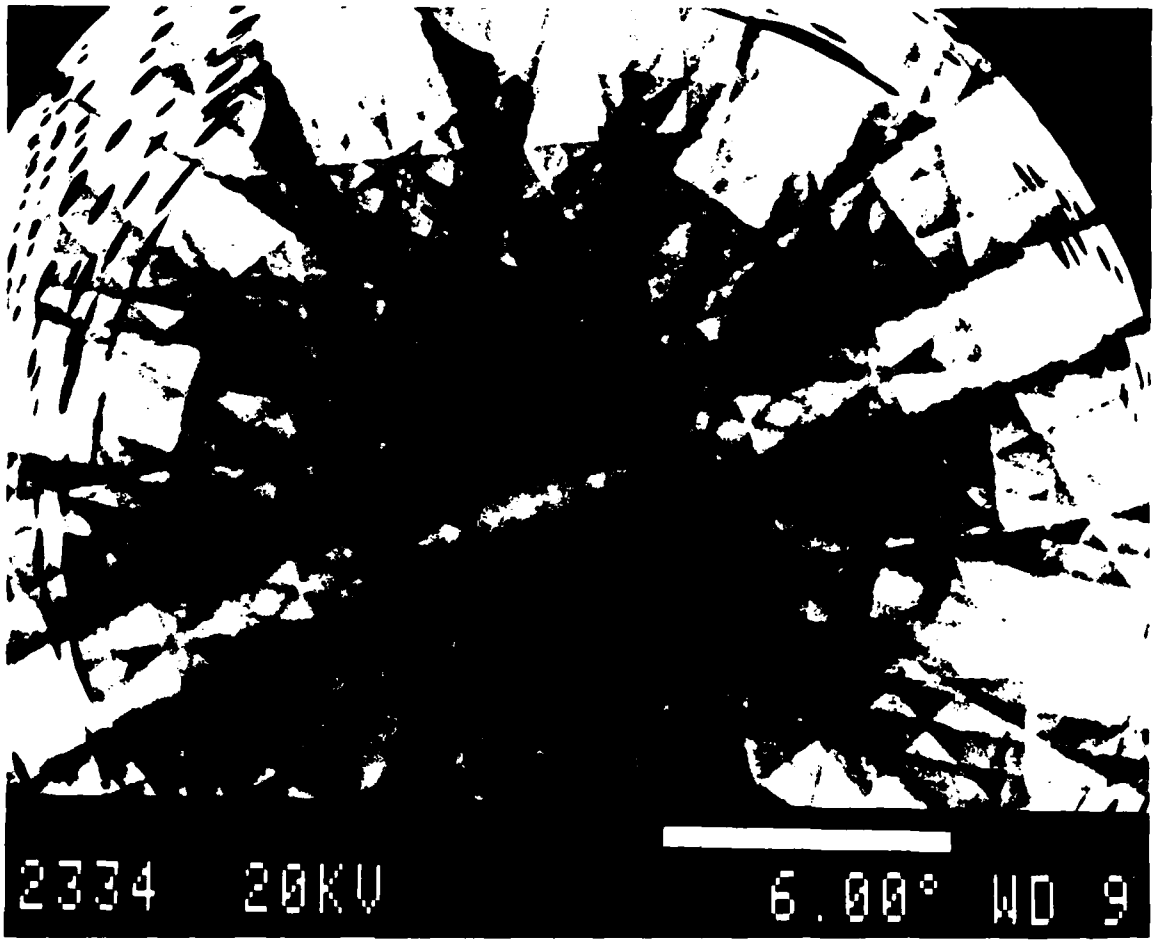


FIGURE 10

{110} ZONE AXIS CHANNELING PATTERN FROM CLEAVED CROSS-SECTION OF SAMPLE #15.

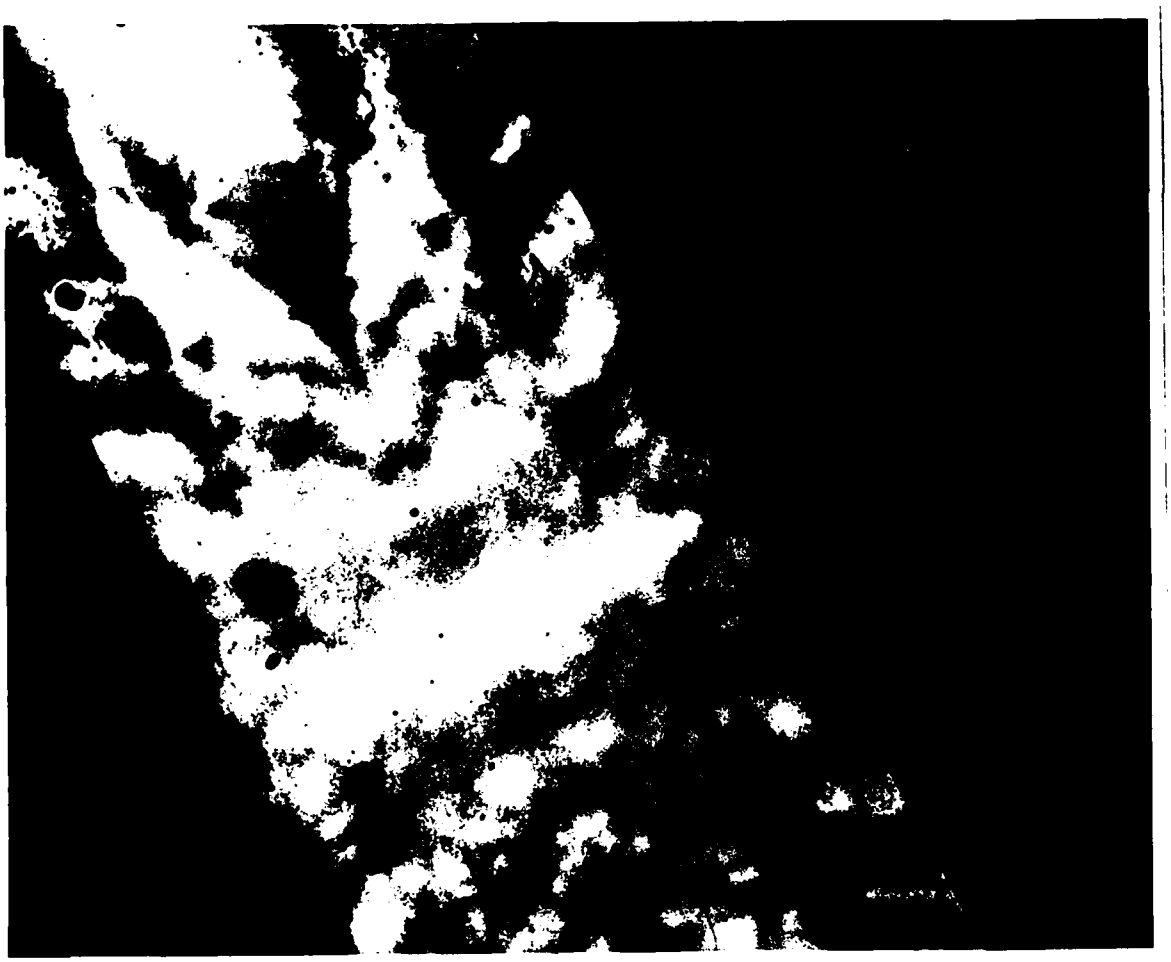


FIGURE 11

HYBRID IMAGE OF THE CROSS-SECTION OF SAMPLE #15. THE SUPERIMPOSED CHANNELING PATTERN CORRESPONDS TO THE CENTRE PART OF THE {110} PATTERN SHOWN IN FIGURE 2.

FIGURE 12

S.E.M. IMAGE OF CLEAVED CROSS-SECTION OF SAMPLE #15 SHOWING THE EPITAXIAL LAYER. NOTE THE HIGH SECONDARY ELECTRON EMISSION.

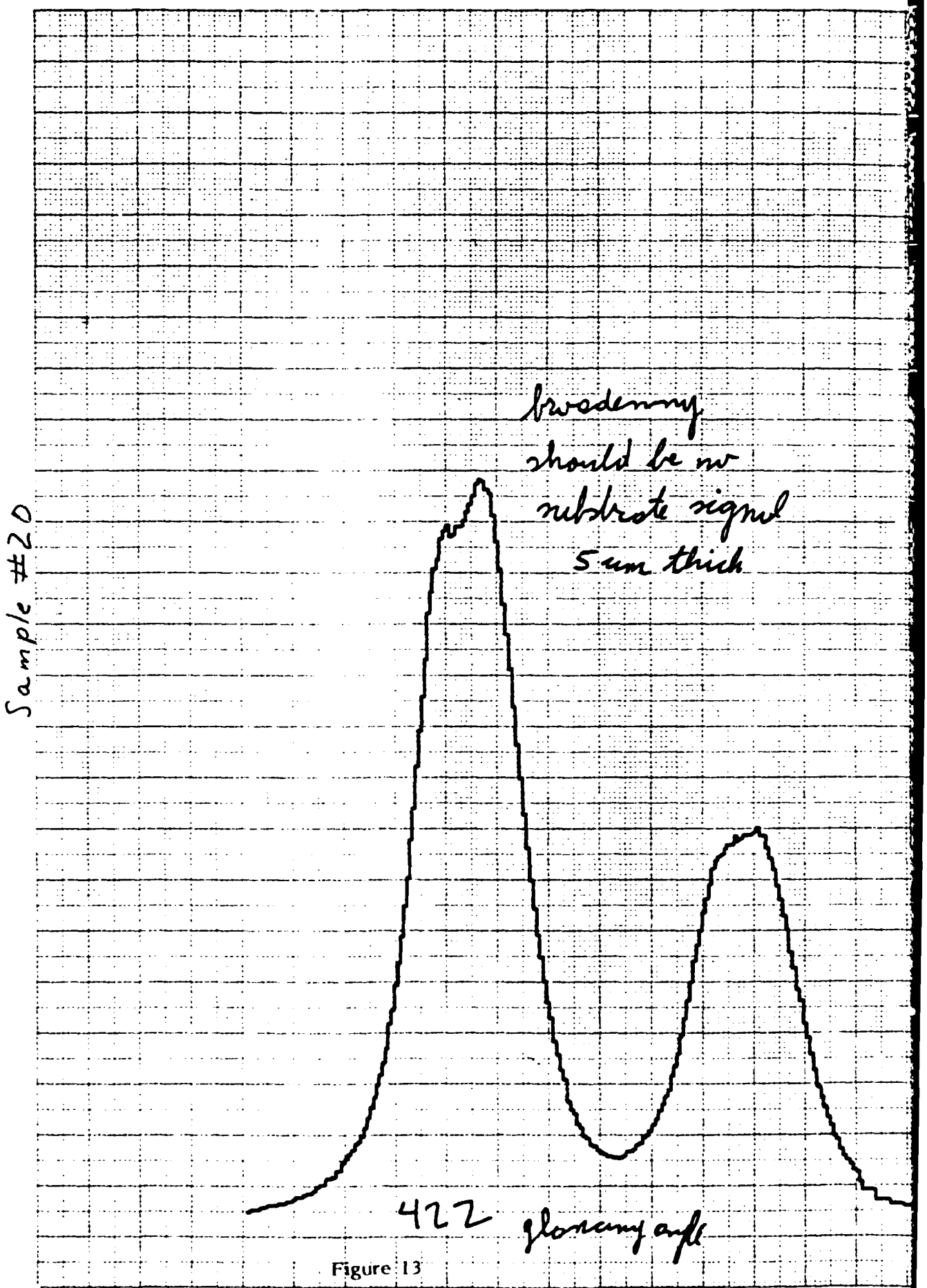

Sample #20
broadening should be no substrate signal 5 um thick
42.2 glancing angle

Figure 13

DATE: 4/17/84

DIFFRACTION CONDITION: $\theta = 42.2$ @ 5°

NAME/WAFER ID: #33 400°C

OPERATOR: 9×10^{-5} Å

this scan is indistinguishable from an as-polished substrate!

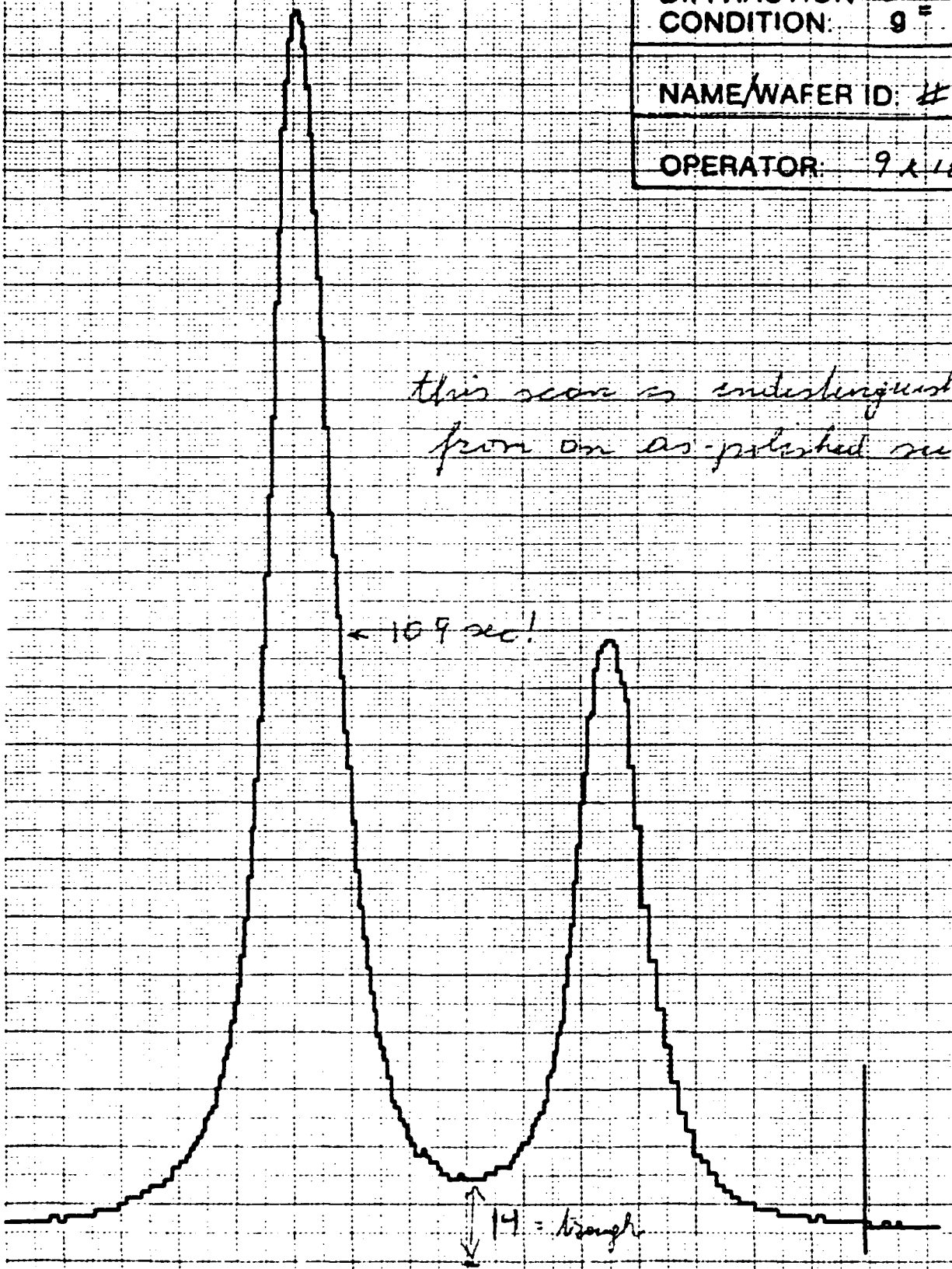


Figure 14

C. Auger Analysis

A Perkin-Elmer PHI 600 scanning Auger microprobe was used for the Auger studies. With the design of the ICB machine, an in-situ Auger system is not possible. Therefore, samples must be analyzed in a second machine. Characterization of the samples were done on the 100 surface as well as the 110 faces of the wafer. For the surface analysis, the samples were raster scanned in a number of places on the wafer with each analysis done after sputtering 80 - 100 Å of material away. A 3 Kev accelerating voltage with a 10na current was rastered over a 100μm X 100μm area as well as a 10 Kev accelerating voltage with a 10na current. An Ar+ ion beam was used to etch the 100 surface at a rate of 14 Å/sec. The change in surface spectra versus depth can be seen in Figures 15, 16, 17, and 18.

A second set of experiments was also run to characterize the 110 face. In this work a sample was fractured in vacuo, and the freshly exposed surface was evaluated. By this method, the surface film was clearly visible, and the substrate and epi film could be analyzed independently on the freshly exposed surface. For this analysis, a 60 Å spot size was used. The intensity ratio of the $GaL_3M_4M_4$ peak (1228ev) to the $AsL_3M_4M_4$ peak (1329 ev) was found to be 1.38 for the epi film compared to the substrate. This compares to the value of 1.41 reported by Van Oostrom[1]. To determine elemental concentrations from the peak intensities, relative elemental sensitivity factors must be defined based on a sample matrix of empirical value. Van Oostrom has determined these factors (5 Kev incident beam energy). For the samples evaluated in this work, the following data were obtained for the 110 faces. Each point was corrected using the factors determined by Van Oostrom: The Auger scans for these values can be seen in Figures 19 and 20.

Substrate	49.5 ± 0.5% Ga	50.5 ± 0.5% As
Epi	48.3%	51.7%

substrate

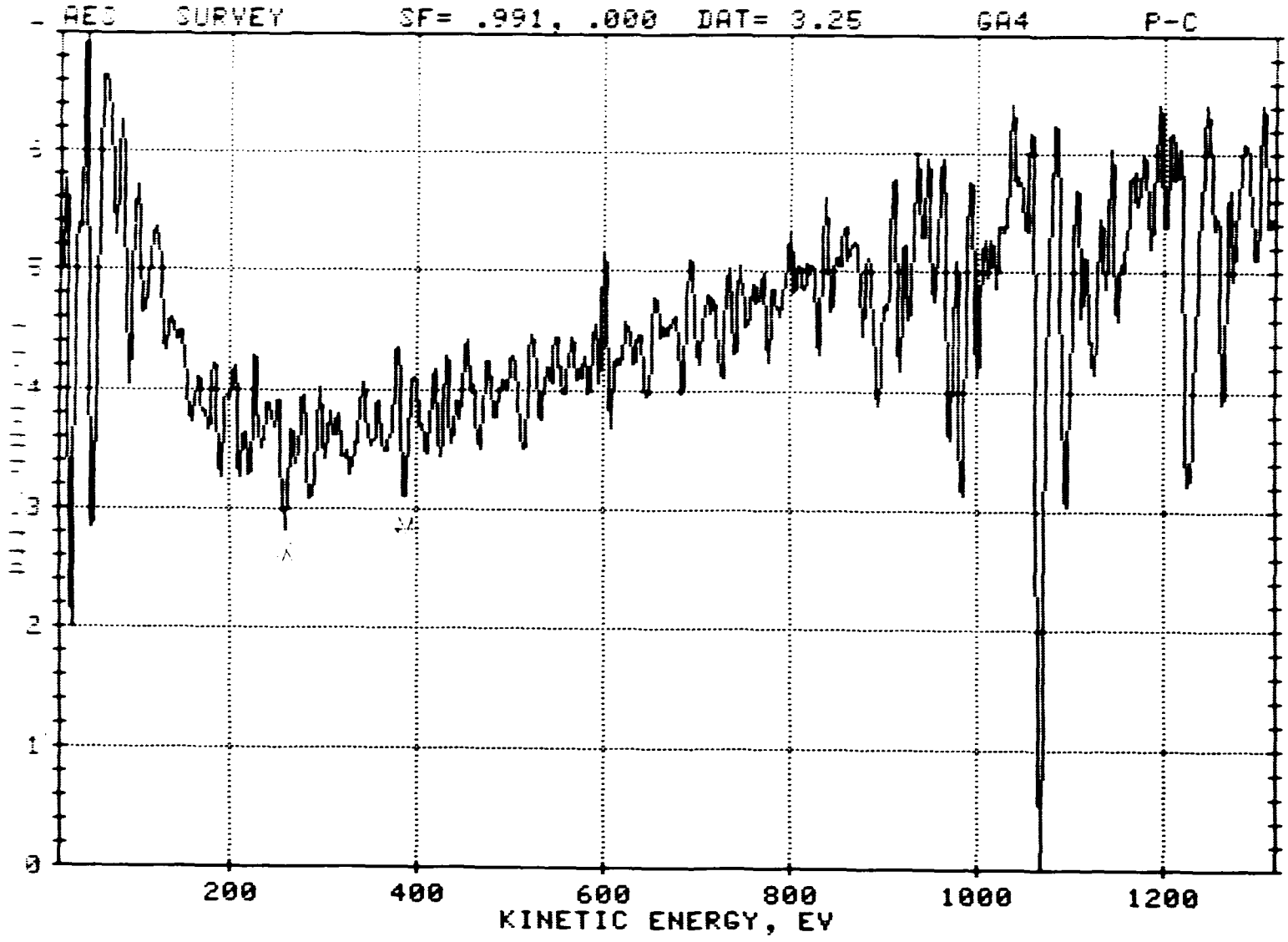


Figure 15

Substrate

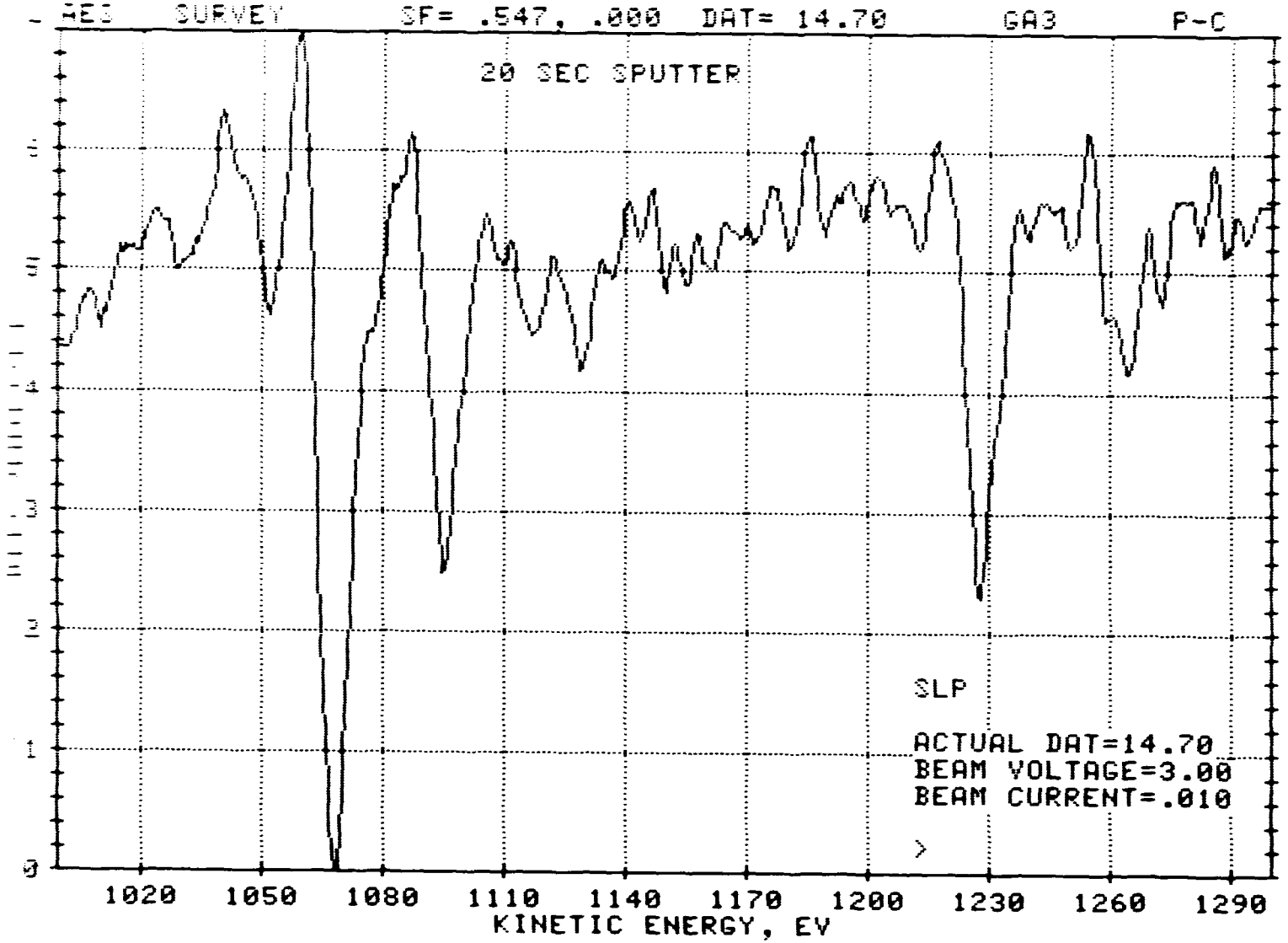


Figure 16

~~Sample #1~~
Substrate

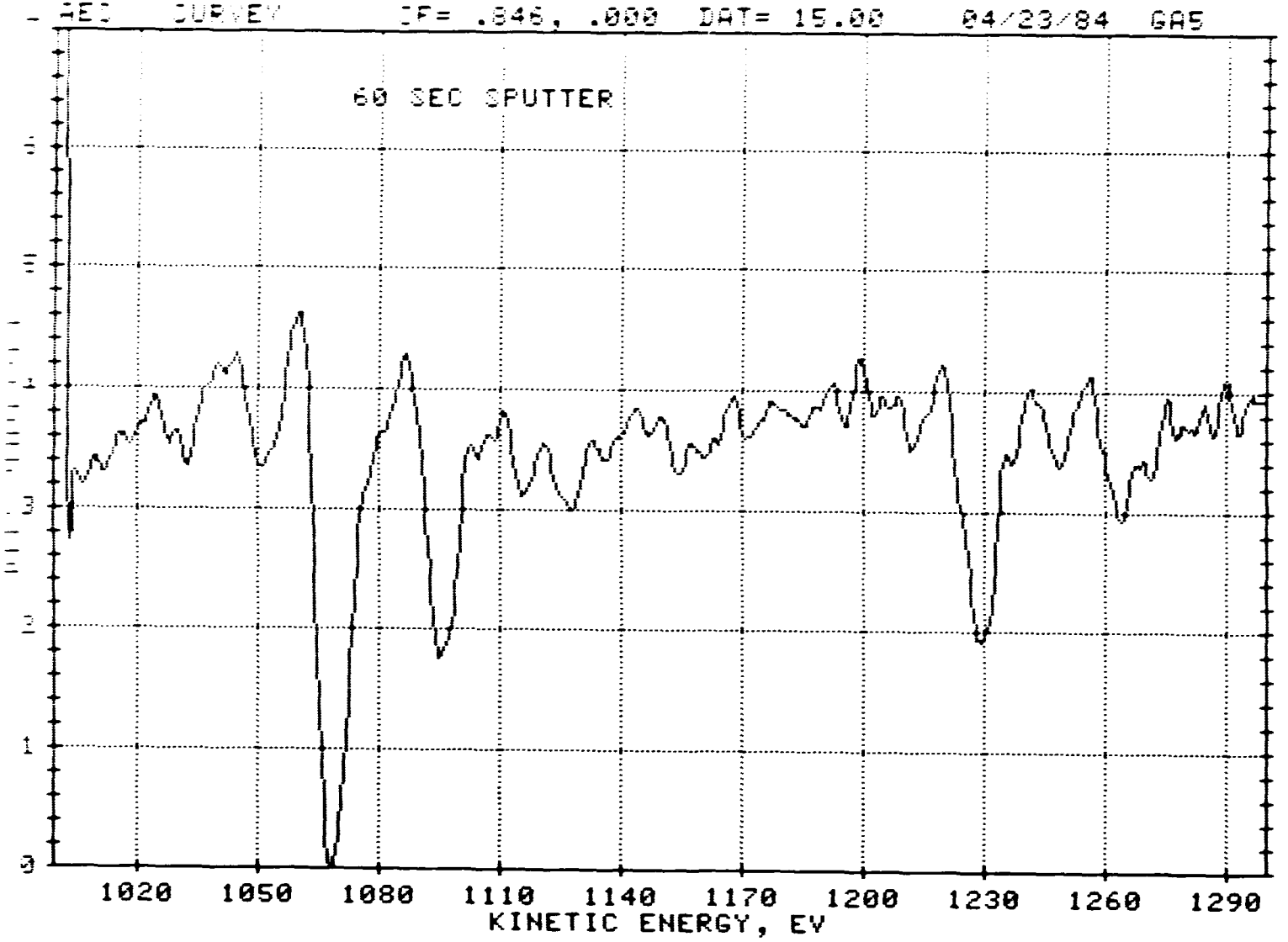


Figure 17

Substrate

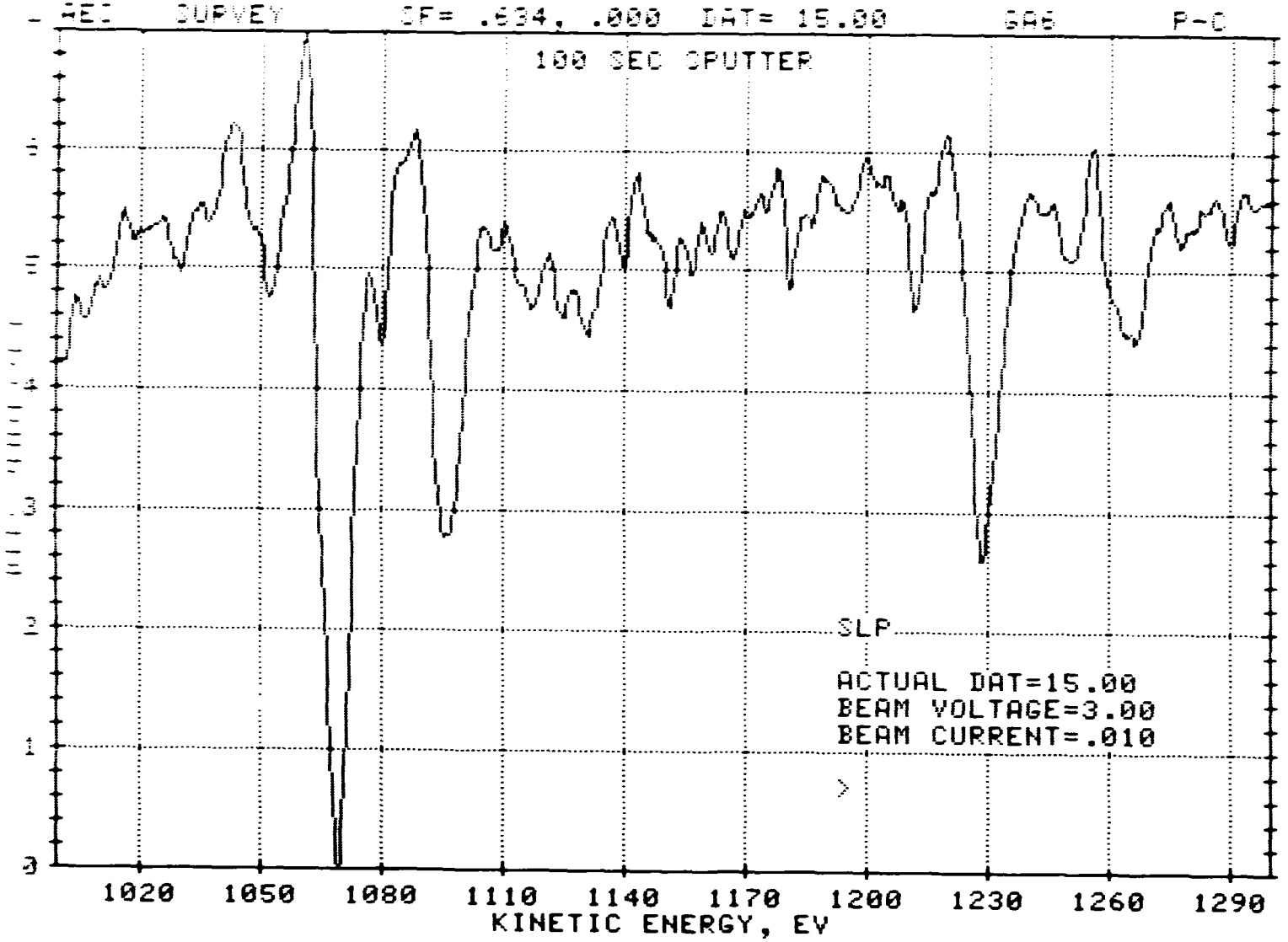


Figure 18

#10 substrate <110>

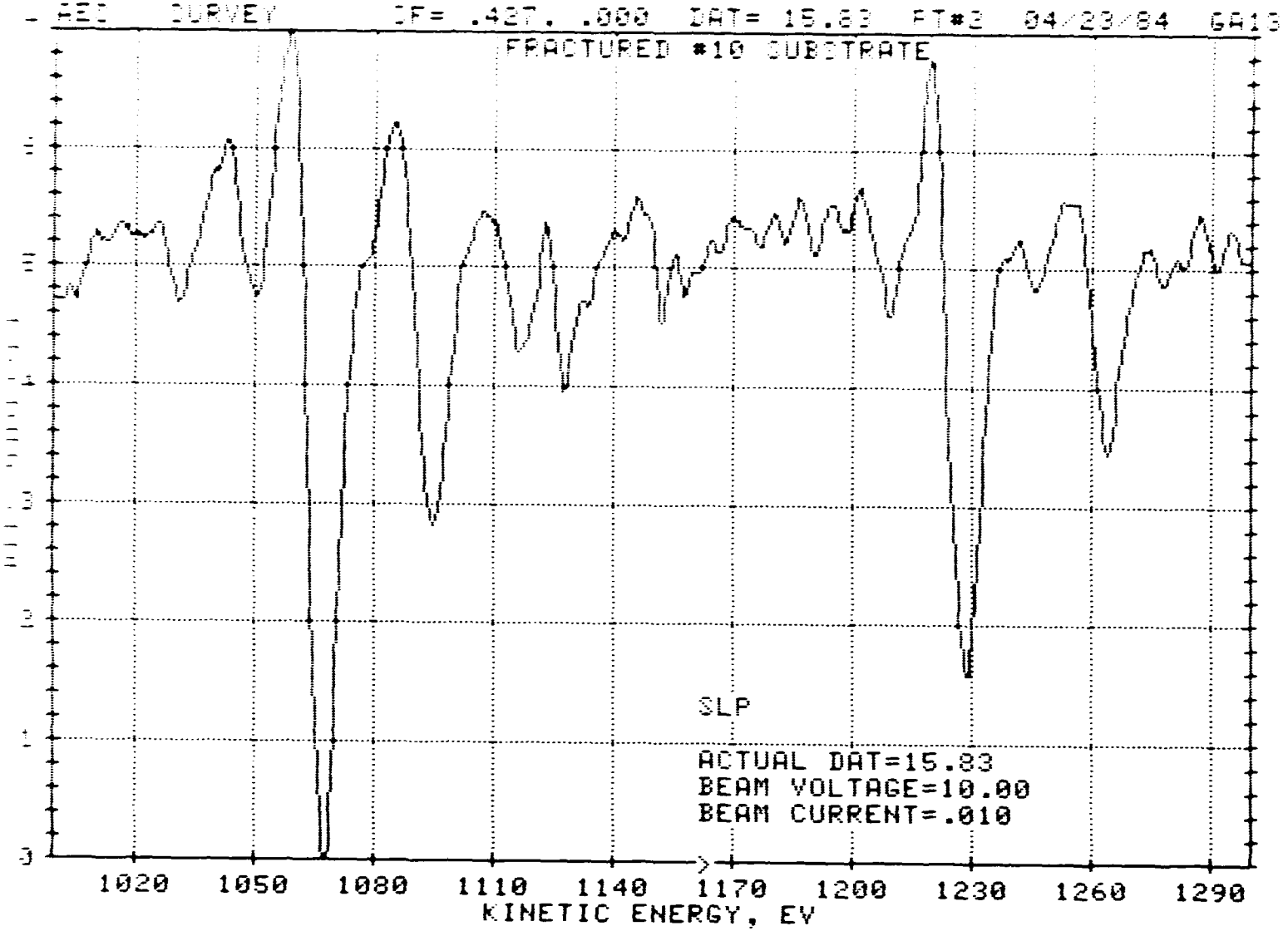


Figure 19

#10 epi film <110>.

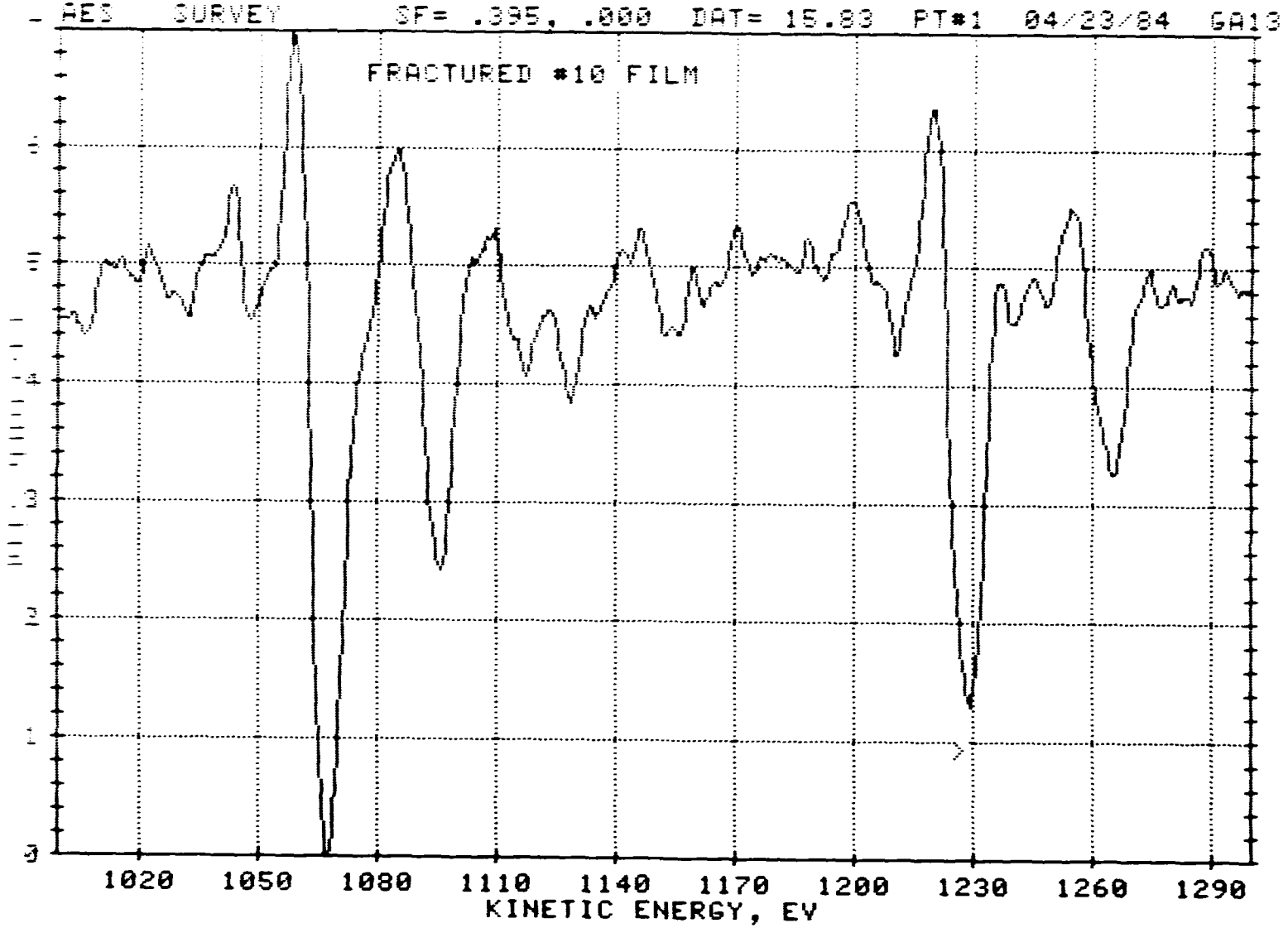


Figure 20

Although the 110 face is expected to contain equal concentrations of Ga and As atoms, a variation of ± 10% is reported due to variations in step densities[2]. Therefore, the results agree very well for both epi and substrate.

Previous work on 100 faces has shown a preferential etching of the arsenic yielding an intensity ratio of 1.8 for Ga/As and a stoichiometry of Ga = 56% and As = 44%[3]. The results obtained on samples grown in this work were:

	I_{GaLMM}/I_{AsLmm}	Ga(At%)	As(At%)
Sample #10	1.90	57.4	42.6
#13	2.02 ± 0.19	58.8	41.2
#15	1.81	56.3	43.7
Substrate	1.95 ± 0.07	58.1	41.9

The Auger spectra for the samples can be seen in Figures 21, 22, 23. In-situ Auger analysis would better resolve surface stoichiometry variations. Once the surface is exposed to the atmosphere, hydrocarbon contamination and surface oxidation alter the concentrations. However, as discussed earlier, this option is not available on the existing hardware. Thus, the in-vacuum cleaving of the sample should produce the most accurate alternative, and this work showed the stoichiometry of the substrate to equal the epitaxial film.

D. Electrical Evaluation: Hall Data and Capacitance/Voltage (C/V) Profiles and Photoluminesence (P/l) Scans

The C/V data for the samples were not meaningful. In each case, there was no change in capacitance as a function of voltage. This was due to the high resistivity of the epi film which caused the depletion layer to extend beyond the epi film and into the substrate. A mercury probe was used for these measurements, and a standard film was used to calibrate the system. When one

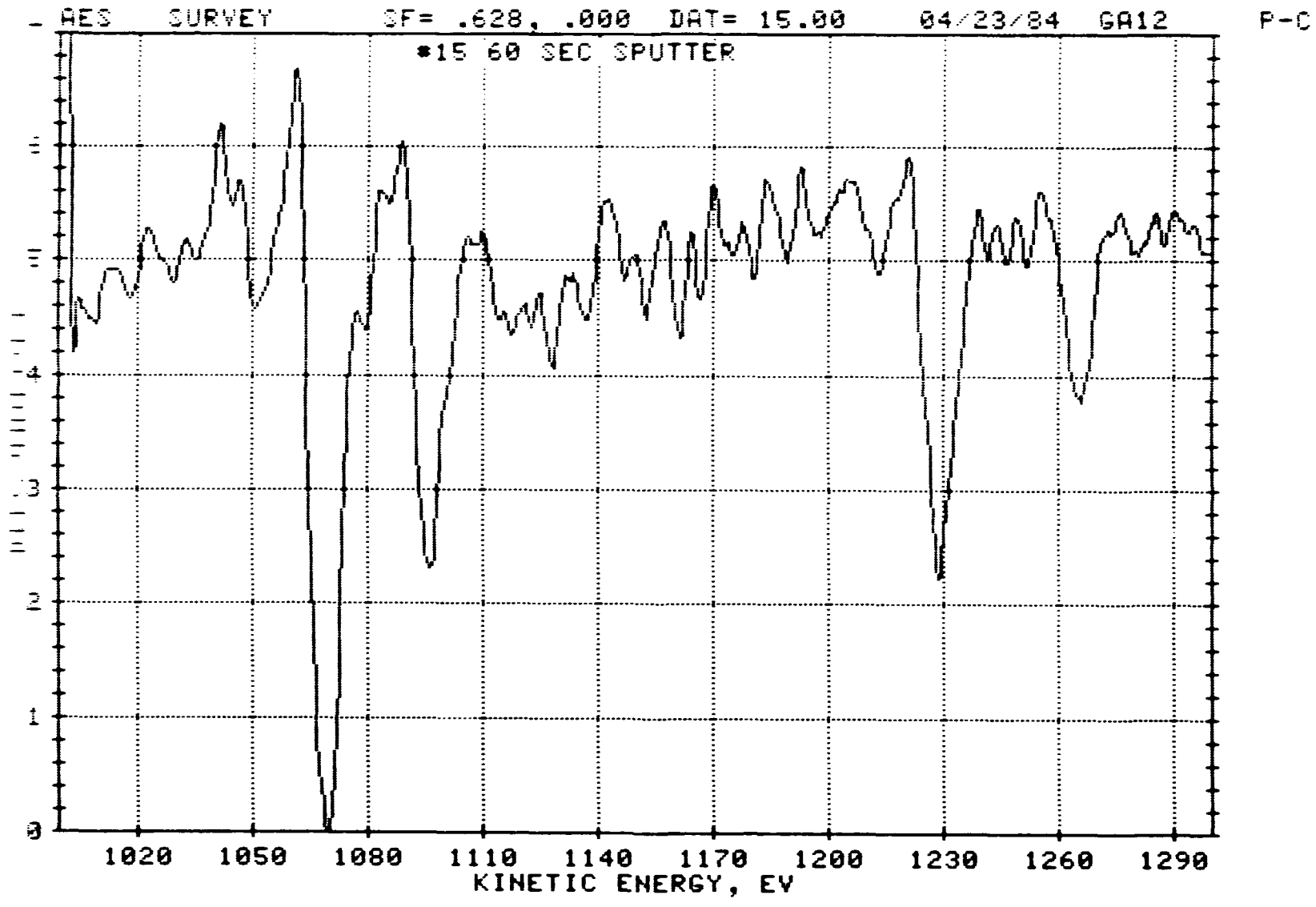

AES SURVEY SF= .628, .000 DAT= 15.00 04/23/84 GA12 P-C
*15 60 SEC SPUTTER
0
1
2
3
4
1020
1050
1080
1110
1140
1170
1200
1230
1260
1290
KINETIC ENERGY, EV

Figure 21

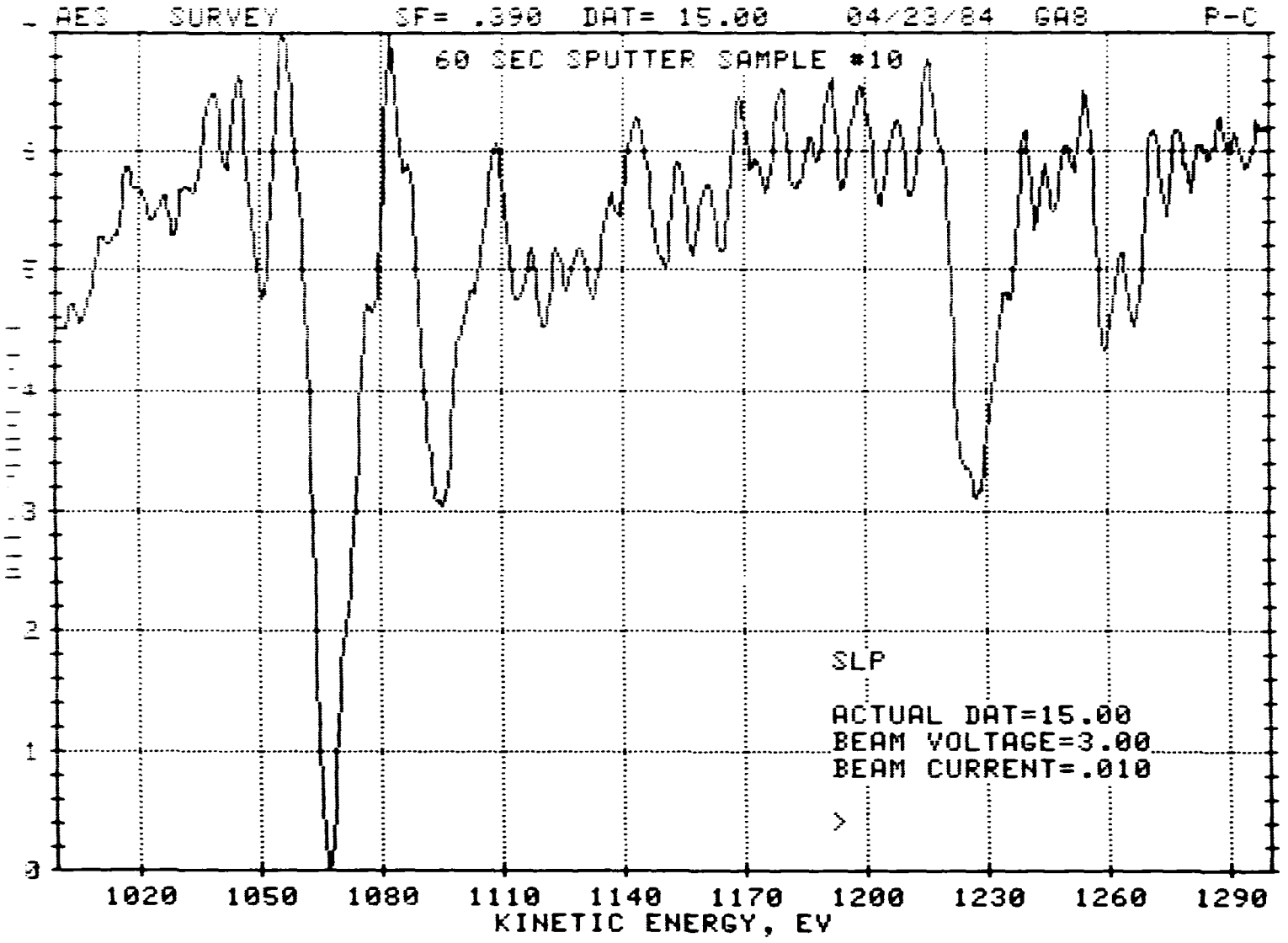

AES SURVEY SF= .390 DAT= 15.00 04/23/84 GA8 P-C
60 SEC SPUTTER SAMPLE #10
SLP
ACTUAL DAT=15.00
BEAM VOLTAGE=3.00
BEAM CURRENT=.010
>
1020 1050 1080 1110 1140 1170 1200 1230 1260 1290
KINETIC ENERGY, EV

Figure 22

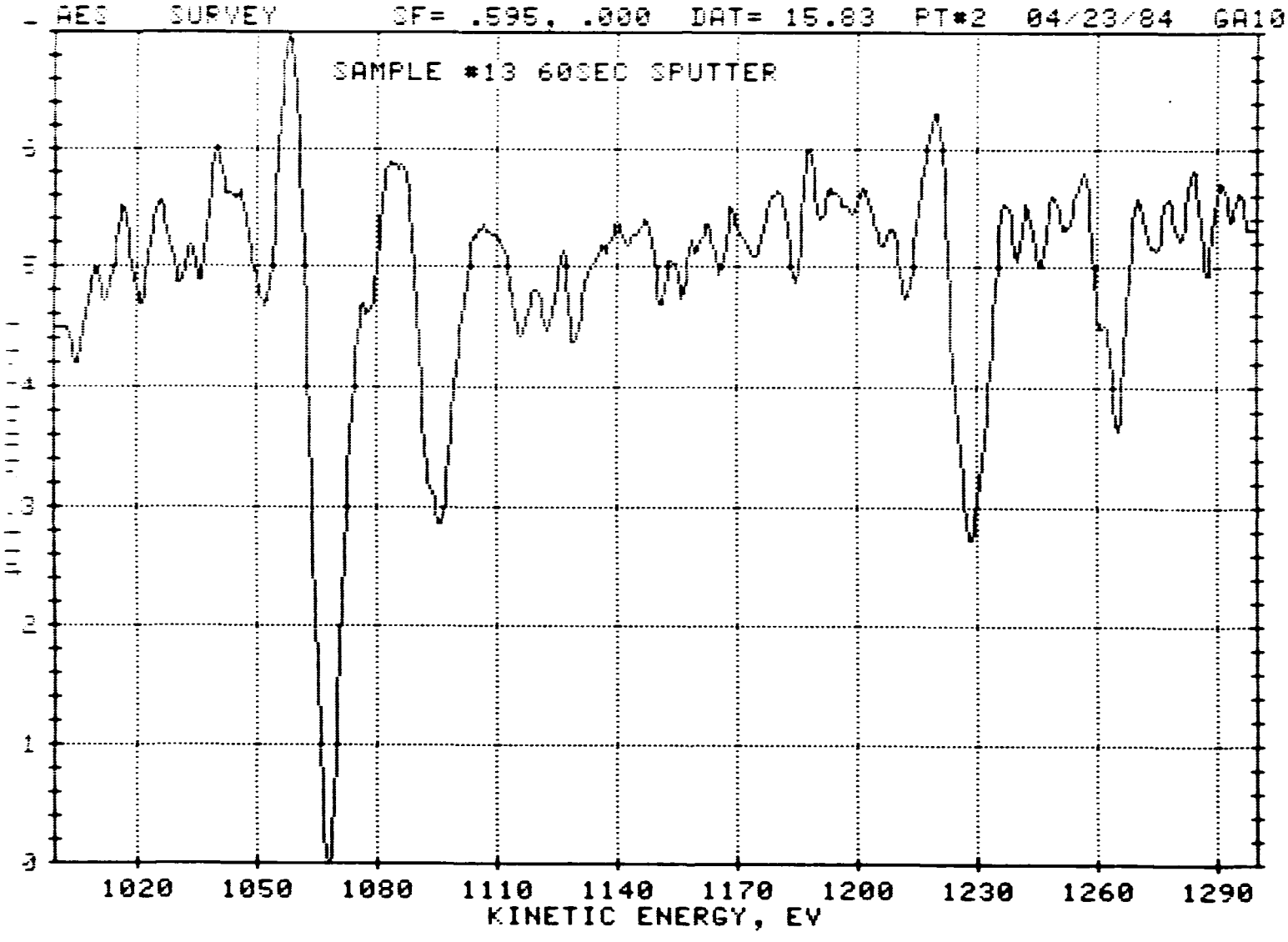

AES SURVEY SF= .595, .000 DAT= 15.83 PT#2 04/23/84 GA10
SAMPLE #13 60SEC SPUTTER
1020
1050
1080
1110
1140
1170
1200
1230
1260
1290
KINETIC ENERGY, EV

Figure 23

compares the Hall data and the lack of a C/V profile, the explanation is very reasonable. Until the films are lower resistivity and thicker, the C/V technique will be of no value.

The Hall data collected on all the samples shows three very consistent trends: 1). High resistivity in the films; 2). n-type conductivity; 3). very low mobility. The samples grown in the second series of runs in March were found to have electrical resistivities of 10^3 ohm-cm, independent of thickness. The last three samples grown with higher arsenic pressure show the low mobility, but a lower resistivity, 400 ohm-cm, and a more ohmic nature. When the leads are reversed on these samples, the values are the same in both directions indicating a very ohmic contact. This is consistent with the x-ray data which show a matched cell size, hence less stress in the films.

Photoluminesence was evaluated on these samples but was very inconclusive. These results are quite consistent with the C/V and Hall data. Because of the lack of meaningful data, P/I was not used extensively. P/I scans for samples #13, 15, 16, and 17 are shown in Figure 24. The general conclusion is that the overall electrical quality of the film is quite poor.

VI. Discussion

Phase I results have demonstrated that the Eaton ICB machine can grow films of GaAs that are single crystal and at temperatures below 400° C. The technique is repeatable from run to run and produces films that are of uniform thickness across samples 0.7" X 0.7". However, the low mobilities and high resistivity indicate major problems. Very recent work at Eaton, combined with the data gathered in this work, possibly offer an explanation for these results.

Work done several years ago by Schiller et al[4] studied the predominant ion actions within different energy regions. A graphic showing these conclusions is shown in Figure 25. The interesting section is that from 1 - 1000 ev per ion. In this region, material with activated centers, i.e. charge defects, structural

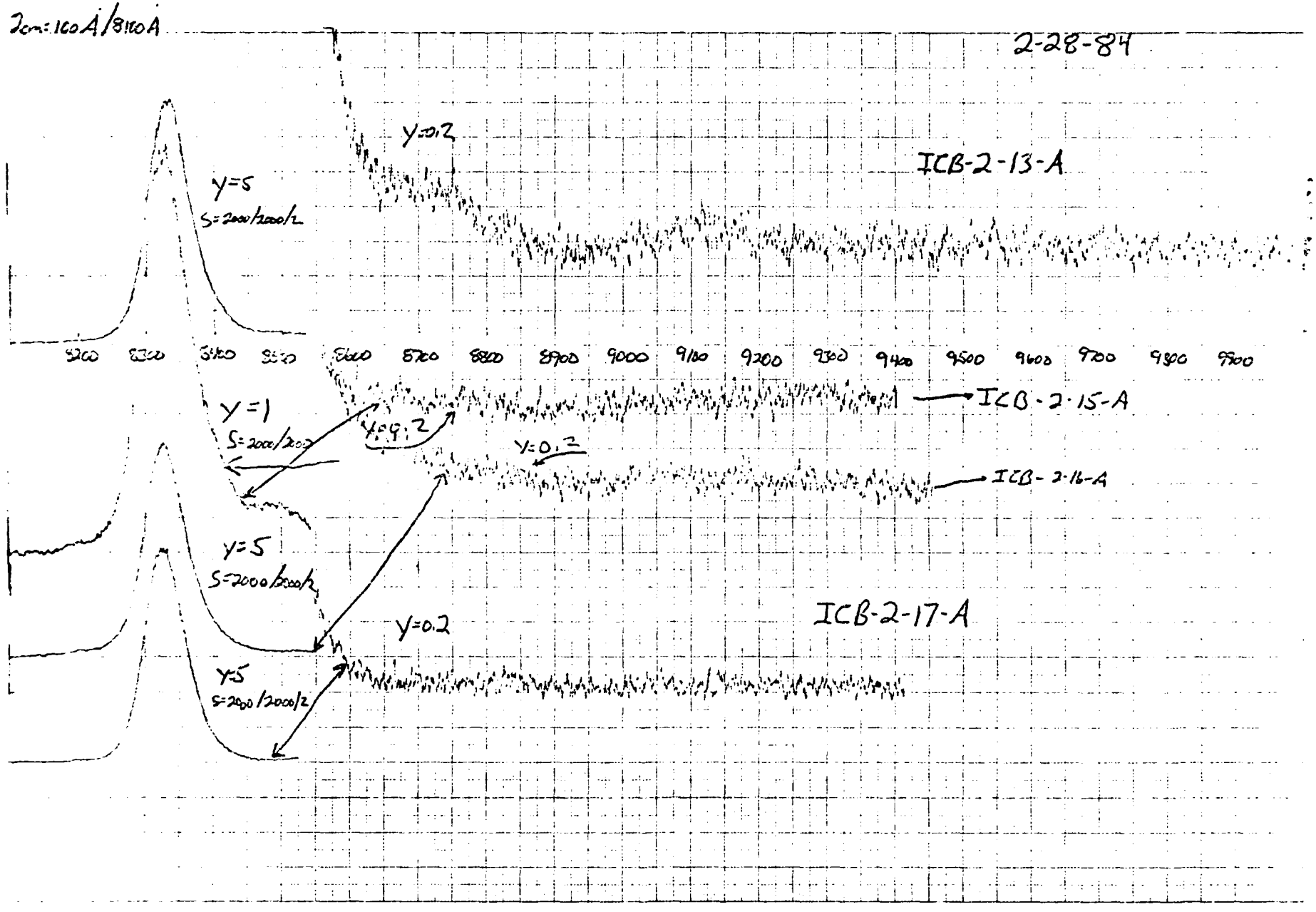
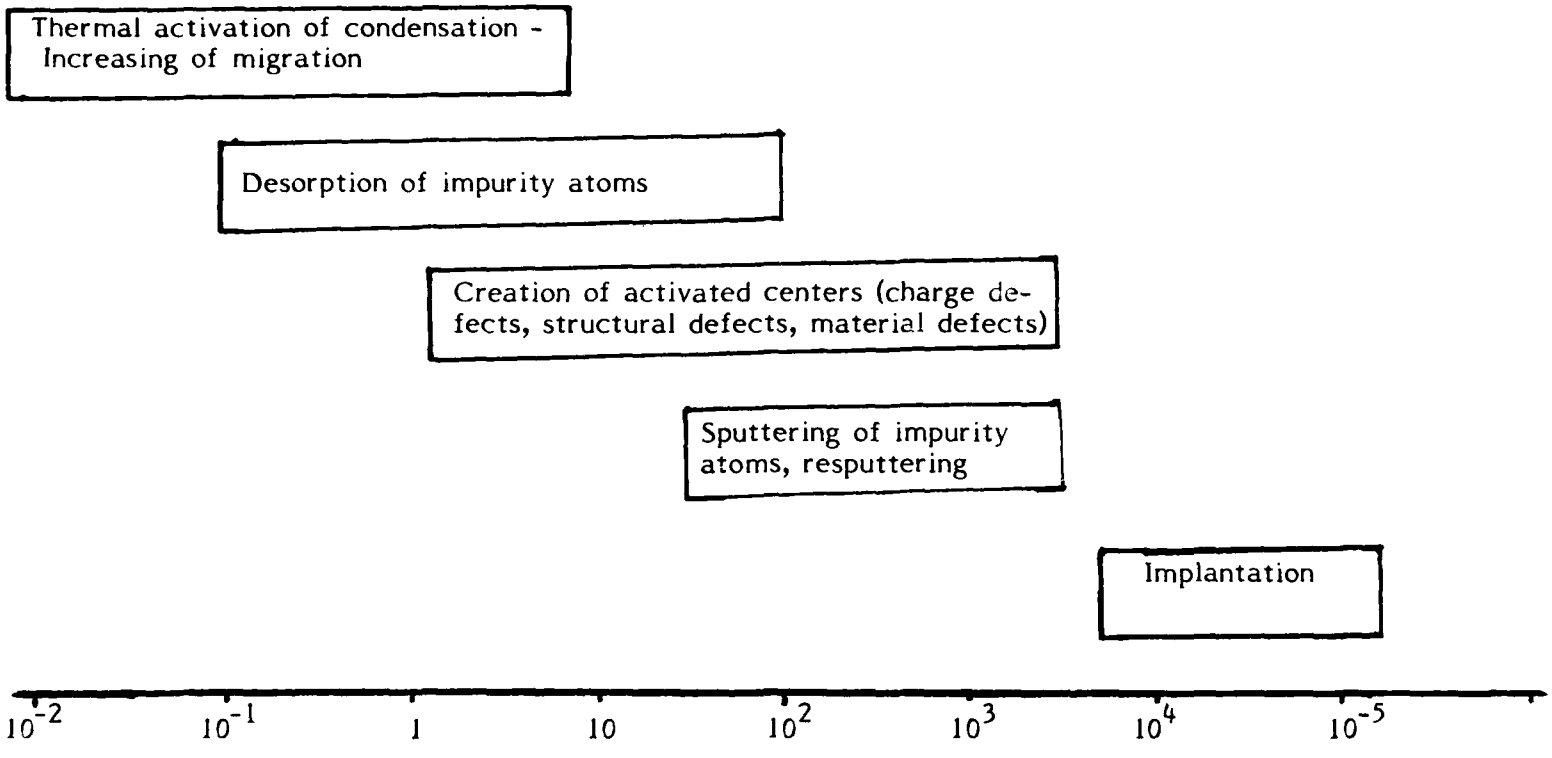

2cm = 100 Å / 8100 Å
2-28-84
Y=0.2
ICB-2-13-A
Y=5
S=2000/2000/2
8200 8300 8400 8500 8600 8700 8800 8900 9000 9100 9200 9300 9400 9500 9600 9700 9800 9900
Y=1
S=2000/2000/2
Y=9.2
ICB-2-15-A
Y=0.2
ICB-2-16-A
Y=5
S=2000/2000/2
ICB-2-17-A
Y=0.2
Y=5
S=2000/2000/2

Figure 24



Predominant Ion Actions Within Different Energy Range

Figure 25

defects and material defects are produced. If there were no clusters found or only clusters with ~10 atoms, the average kinetic energy of the ionized/accelerated ions (assuming 3 Kev acceleration potential) would be in the range of 300 ev. At this range, one would expect single crystal material, but with poor electrical properties due to the multitude of native defects. This structure would indeed be expected to have very low mobility and high resistivity. Even on those samples having a correct lattice constant, the impinging energy is great enough that the defect structure is still the dominant mechanism.

Work at Eaton subsequent to the last set of experiments has shown that there is little or no cluster formation from crucibles that are not uniformly heated. Rather, droplets accumulate in the crucible, particularly at or near the nozzle area. This is consistent with the observations made when the gallium cap was removed. Further work at Eaton with the newly designed radiant sources, show enhanced heating uniformity and, indeed, the formation of clusters. However, the cluster size was still less than the 1000 - 2000 atoms Takagi quotes for standard cluster size. Work is now proceeding to improve heating uniformity and to lengthen the nozzle area from 1mm to 10mm to enhance the number of collisions in the nozzle area.

The combination of the efforts does, in the opinion of the author, explain the data obtained, both electrical and physical. By having very small aggregates or only ionized beams, the kinetic energy is too great at the surface and the native defects are readily formed.

As with any new hardware and technology, a great deal has been learned from a few experiments. The limited results obtained thus far appear very encouraging as to the viability of ICB for producting acceptable quality single crystal epi films. Current work on the machine coupled with improved process understanding should move the technology rapidly.

VII. Acknowledgments

Dr. Adams would like to express his sincere thanks to a number of people and organizations who helped collect data and contributed many fruitful comments relating to data interpretation. Drs. Creber and Ball of Alcan International supplied the Auger and channeling data; Dr. D. Look of AFWAL the Hall data; and Dr. W. Wagner of Bell Labs supplied the x-ray data. Thanks also go to Mr. R. Potter of Motorola for the use of his evaluation facility and Mr. T. Robertson for valuable discussions.

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