$Ga_xIn_{1-x}P$/GaP HETEROSTRUCTURES ON Si(001) SUBSTRATE

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ABSTRACT

In this contribution we report on the real-time monitoring of low temperature growth of epitaxial $Ga_xIn_{1-x}P$/GaP heterostructures on Si(100) by pulse chemical beam epitaxy, using tertiary butylphosphine (TBP), triethylgallium (TEG), and trimethylindium (TMI) as source materials. Both step-graded and continuously graded heterostructures have been investigated. The composition of the $Ga_xIn_{1-x}P$ epilayers has been analyzed by various techniques including X-ray diffraction, Rutherford backscattering, Auger, and Raman spectroscopy. Good correlation has been found between X-ray diffraction, RBS, and Vegard's law compositional analysis. We used P-polarized Reflectance Spectroscopy (PRS) and Laser Light Scattering (LLS) to monitor the growth rate and surface morphology during growth. The information gained by these techniques has been utilized in the improvement of the surface preconditioning as well as to optimize the initial heteroepitaxial nucleation and overgrowth process. We studied the optical response to the compositional changes in the surface reaction layer (SRL) during the exposure of the surface to either sequential or synchronous pulses of TEG and TMI. The cross sectional TEM analysis indicates that the synchronous exposure results in an abrupt $Ga_xIn_{1-x}P$/GaP interface while the sequential exposure does not which may suggest a compositionally graded interlayer formation. For heteroepitaxial $Ga_xIn_{1-x}P$ films on Si, a buffer layer of GaP is found to be necessary for optimum uniformity of the $Ga_xIn_{1-x}P$ layer. The selective growth of $Ga_xIn_{1-x}P$ on Si(001) is accessed.

INTRODUCTION

The epitaxial growth of polar semiconductors on nonpolar substrates has been investigated mainly because of its importance in microelectronic device fabrication. The improvement in performance and reliability of such devices is generally tied to defect formation and propagation in the epilayer. In order to improve the epilayer, substrate materials are selected for high purity and perfection. This is because imperfection on substrate propagates on the grown epilayer, as we have shown previously [1]. As a result of the advanced state of silicon technology, epitaxial growth on silicon wafers has been investigated mainly because silicon is readily available free of defect, with high purity and low cost. The advances in silicon based industry makes silicon a unique substrate through the provision of high quality heteroepitaxial buffer layer to other applications requiring compound semiconductors. However, the key issue is of the structural imperfections in epilayers.

Structural defects are too common in heteroepilayer containing point, line, and planar defects whose origin is generally explained in terms of lattice strain and chemical incompatibilities in the early stages of heteroepitaxial overgrowth [2]. Numerous studies have been done to try to understand the formation of defects in compound films [3-8]. The heteroepitaxial overgrowth of silicon by nearly lattice-matched compound semiconductors has been investigated in the context of the separation of the chemical problems associated with the initial sealing of the silicon surface by a contiguous epitaxial compound film from the problems associated with the generation of strain during heteroepitaxial growth [2,6,7]. The control of planar defect formation during the initial period of nucleation and overgrowth has been a key issue in the epitaxial overgrowth of Si by a nearly lattice-matched compound. Planar defect formation on the basis of mismatch stresses is no longer considered a major contributing factor in the case of nearly lattice-matched epitaxial overgrowth of Si when low temperature growth processes are used, such as chemical beam epitaxy [9] and metal organic chemical-vapor deposition [6]. For the low temperature growth of nearly lattice-matched GaP on Si, the defect formation is now believed to be related to the chemical interactions on silicon surface in the very early stages of epitaxial overgrowth [6,2]. These interactions may contribute to errors in stacking, thus introducing planar defects in the growing layer. In order to gain understanding on chemical interactions, real-time process monitoring must be integrated into the growth process to develop understanding of the nature of these interactions.

In this paper, we present results on the real-time monitoring of low temperature growth of $Ga_xIn_{1-x}P$ by pulse chemical beam epitaxy with real-time monitoring tools including p-polarized reflectance spectroscopy and laser light scattering. The advantage of growing a buffer layer of lattice-matched (GaP) compound that seals the silicon surface followed by the growth of a mismatched $Ga_xIn_{1-x}P$ compound has been assessed.

EXPERIMENTAL

The PR and LLS data are obtained simultaneously to monitor heteroepitaxial film growth under pulsed chemical beam epitaxy conditions. That is, the surface of the substrate is exposed to pulsed ballistic beams of tertiarybutyl phosphine [TBP, $(C_4H_9)PH_2$], triethylgallium [TEG, $Ga(C_2H_5)_3$], and trimethylindium (TMI) at typically 350-400°C to accomplish nucleation and overgrowth of the silicon substrate by an epitaxial film. The schematic representation of the experimental arrangement for the system has been presented elsewhere [11]. All signals are processed through phase sensitive lock-in amplifiers and registered in real-time by a computer which also controls the pulsing of source materials with 10 Hz resolution. The nonspecularly scattered intensity is detected by a photomultiplier tube (PMT) located 45° form the plane of incidence. The fluxes of the precursor and hydrogen are established by mass flow controllers and are directed via computer-controlled 3-way valves to either the reactor chamber or a separately pumped bypass chamber. This allows the sequential exposure of the substrate to individual pulses of the precursor molecules. The switching of the sources is synchronized with the data acquisition of the PR and LLS signals to correlate the changes in the reflected intensity to the changes in the optical properties of the heteroepitaxial stack that encompass chemistry-induced changes in the surface composition and changes due to the thickness and optical properties of the epitaxial film. $Ga_xIn_{1-x}P$ layers on Si(001) are grown with and without a thin buffer GaP layer. A growth cycle time of 3 seconds is used for the growth of GaP buffer layer and for the synchronous exposure to TEG and TMI for $Ga_xIn_{1-x}P$ growth. We used a total growth cycle time of 6 seconds for $Ga_xIn_{1-x}P$ grown with sequential exposure of TEG and TMI. This consists of a 3 second TBP-TEG cycle sequence followed by a 3 second TBP-TMI cycle sequence. Prior to growth the silicon wafer substrate was RCA cleaned followed by a buffered HF dip and water rinse. Typical growth rates under the chosen pulsed chemical beam epitaxy (PCBE) growth conditions are in the order of 1Å/sec.

RESULTS AND DISCUSSION

The PR and LLS responses during $Ga_xIn_{1-x}P$ heteroepitaxial growth are shown in Fig. 1 and Fig. 2, respectively for direct growth on silicon and on GaP buffer layer under condition of simultaneous exposure to TEG and TMI. After a preconditioning time of 600 s, the film growth is initiated with precursor sequence consisting of TBP pulse range of 0.0-0.8 sec and combined TEG/TMI pulses range of 1.5-1.8 sec within a total cycle time of 3 seconds. The PR signal is a sensitive function that depends on changes in the dielectric response of the sample. This may be a temperature-induced change in the dielectric function of the substrate, a chemical modification or roughening of the surface, or an overgrowth by a thin film having a dielectric function that differs from that of the substrate. The LLS signal measures the radiation scattered by rough sample interfaces and bulk defects and is a good measure of surface morphology during growth. As the epilayer grows, the PR signal oscillates as a result of the interference with the substrate interface. The contribution of an additional interface to the measured interference oscillation can be observed in real-time, as for instance in the case of $Ga_xIn_{1-x}P$ growth on GaP buffer layer, as illustrated in Fig. 2 after a process time of 1200 sec. Such contribution was not apparent in the case of the exposure of the surface to sequential pulses of TEG and TMI, leading to the stipulation for a transient graded layer in this case.

A crucial issue in the growth of high quality GaP epilayer on silicon is the initial nucleation stage which introduces three dimensional island growth. As recently shown, PR and LLS can be used to obtain information about the early stage of nucleation and overgrowth [10]. In Fig. 1, we observed that the scattered intensity increases monotonically and immediately after the nucleation of $Ga_xIn_{1-x}P$ layer on silicon. This implies significant surface roughening and three dimensional growth which most likely would be accentuated as a result of the polar/nonpolar growth and/or the

Figure 1:

Real-time monitoring of $Ga_xIn_{1-x}P$ growth on silicon with simultaneous exposure to TEG and TMI

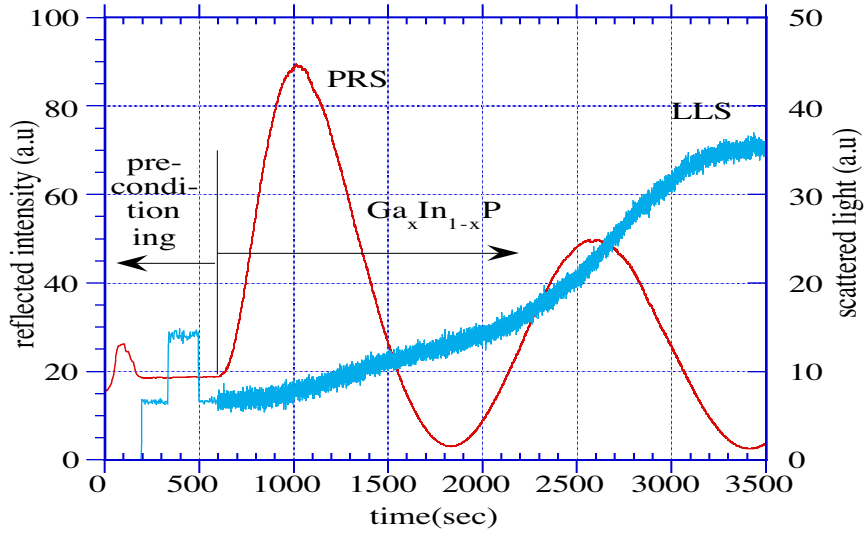


Figure 2:

Real-time monitoring of $Ga_xIn_{1-x}P$ growth on silicon with simultaneous exposure to TEG and TMI

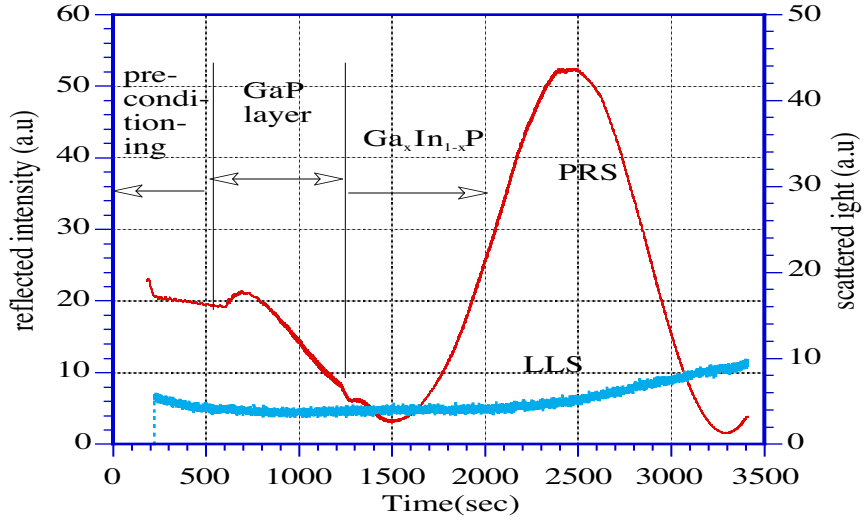


Figure 3

Indium concentration in $Ga_xIn_{1-x}P$ as a function flow ratio (TMI:TEG)

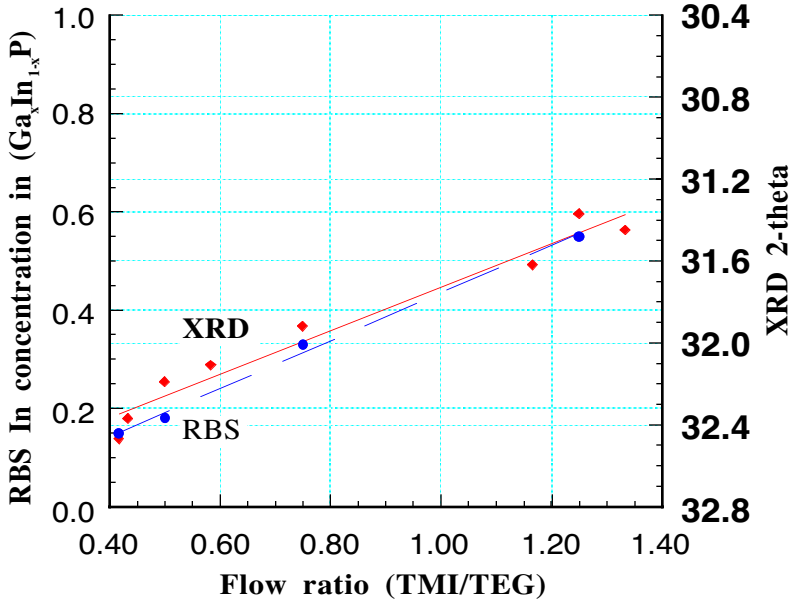
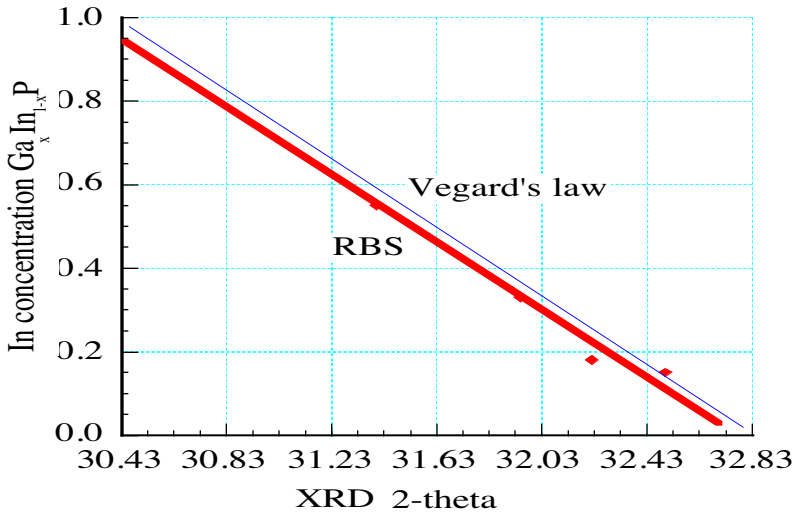


Figure 4.

Compositional analysis of $Ga_xIn_{1-x}P$ by RBS and XRDas compared to Vegard's law



composition increases from x=0 to x=1.0. In comparison, in the growth of nearly lattice-matched lattice mismatch between Si and $Ga_xIn_{1-x}P$ which varies form 0.39 % to 8 % as the indium GaP/Si the LLS signal, as illustrated in Fig. 2, remains constant well beyond the transition to $Ga_xIn_{1-x}P$ layer growth. This implies that the mismatch parameter $\Delta a/a$ is a major contributing factor that influences the growth mechanism in the early stage of epitaxial layer growth.

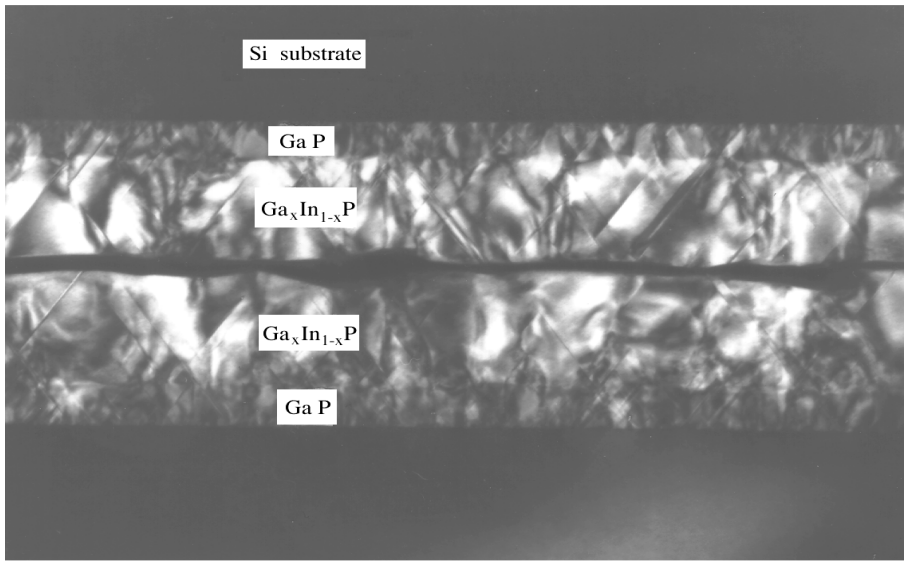
The composition of the as-grown layer are analyzed by X-ray diffraction (XRD), Rutherford backscattering (RBS), Auger (AES) and Raman spectroscopy. The lateral compositional uniformity of the film was evaluated by Raman spectroscopy. The best concentration prediction agreement has been observed between RBS and XRD. Fig. 3 shows the flow ratio (TMI:TEG) as a function of indium concentration in $Ga_xIn_{1-x}P$ as determined by RBS and XRD. The RBS and XRD data from the (200) reflection are in good agreement. Thus the flow ratio can be used to target a particular layer stochiometry. As illustrated in Fig. 4 the compositional analysis of $Ga_xIn_{1-x}P$ by RBS and XRD obeys Vegard's law within their error tolerances.

The structural analysis by cross sectional TEM of the $Ga_xIn_{1-x}P$ layer grown with simultaneous exposure to TEG and TMI shows an abrupt $Ga_xIn_{1-x}P$/GaP interface while layers grown with sequential TEG and TMI exposure does not. Figure 5 shows TEM dark field 220 reflection image of $Ga_xIn_{1-x}P$ layer grown on a buffer layer of GaP on silicon with (a) simultaneous and (b) sequential surface exposure to TEG and TMI. It can be observed that the $Ga_xIn_{1-x}P$/GaP interface is apparent in the case of simultaneous TEG/TMI exposure (Fig. 5a) while not apparent in the case of sequential exposure to TEG/TMI pulses. This is predicted in real-time monitoring by the change in the PR signal resulting from the additional interface as seen in Fig. 2. Planar defects in the case of sequential surface exposure growth (Fig. 5b) appear to propagate through the top surface of the film. In the case of simultaneous surface exposure growth from TEG and TMI, the delineated GaP buffer layer (Fig. 5a) shows higher defect density than the $Ga_xIn_{1-x}P$ layer. A relaxed buffer layer structure can thus be optimized for controlling defect formation.

Planar defects are also known to occur as a result of the coalescence of nuclei overgrown on impurities [10]. This may occur as a result contamination of the surface during sample preparation or precondition of the surface. We investigated the growth selectivity of Ga_xIn_{1-x} P on silicon. Figure 6(a) shows the surface of a sample after growth of $Ga_xIn_{1-x}P$/GaP on Si(001), where the Si surface was partially contaminated by oxygen and carbon patches. Figure 6(b) is an enlargement of one of the contaminated regions. A semiquantitative elemental mapping (Fig.7) for (a) phosphorus, (b) gallium, (c) indium, (d) carbon, (e) oxygen, and (f) silicon shows that the hollow around the $Ga_xIn_{1-x}P$ island (Fig. 6b) is clearly a contaminant on the surface containing carbon (Fig.7d) and oxygen (Fig. 7e). It is clear from the SEM micrograph contrast of Fig. 6 and from the elemental analysis of Fig. 7 that no growth occurred in the carbon and oxygen contaminated region. Only carbon, oxygen, and silicon are detected. Growth of $Ga_xIn_{1-x}P$/GaP on contaminated region will require a higher supersaturation of the precursors for nucleation than for epitaxial growth on a clean surface.

Figure 5:

(a) Transmission electron dark field 220 reflection image of $Ga_xIn_{1-x}P$/GaP on Si(001), using simultaneous TEG/TMI exposure during $Ga_xIn_{1-x}P$ growth.



(b) Transmission electron dark field 220 reflection image of $Ga_xIn_{1-x}P$/GaP on Si(001) using sequential TEG/TMI exposure during $Ga_xIn_{1-x}P$ growth.

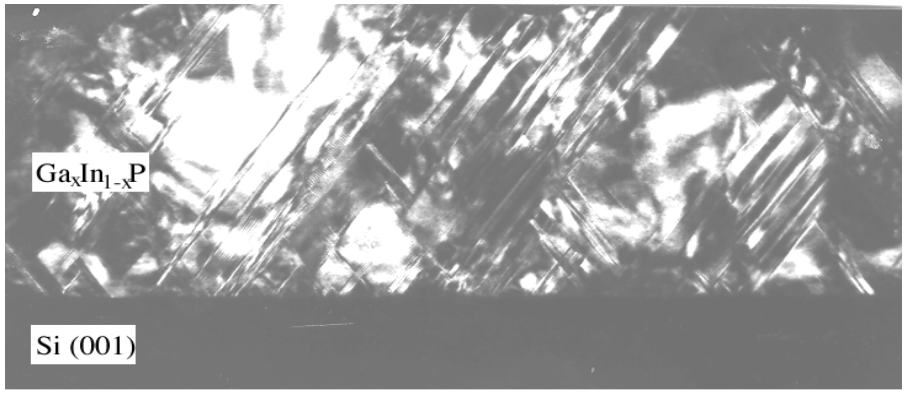
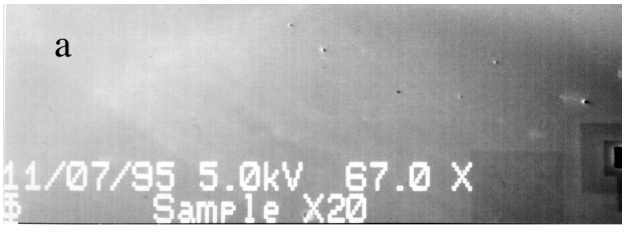
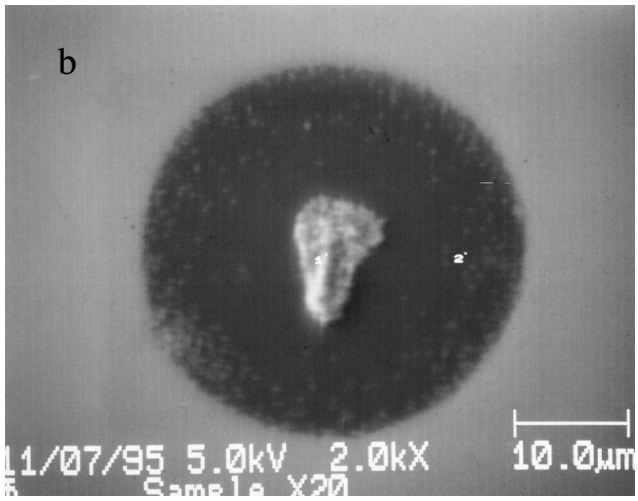


Figure 6:

(a) Scanning electron microscopy of patches in the GaInP layer grown on a partially oxygen and carbon contaminated Si surface.

(b) enlargement of a contaminated region.





CONCLUSION

In this contribution we investigated the growth of step-graded and continuously graded heteroepitaxial $Ga_xIn_{1-x}P$/GaP epilayers on Si(001) by pulsed chemical beam epitaxy, using TBP, TEG, and TMI source materials. The composition of the $Ga_xIn_{1-x}P$ epilayers are analyzed by XRD, RBS, AES, and Raman Spectroscopy. Good correlation has been found between XRD, RBS and Vegard's law compositional analysis. Cross sectional TEM analysis shows that the simultaneous TMI and TEG exposure results in an abrupt $Ga_xIn_{1-x}P$/GaP interface while for sequential TEG and TMI exposure no clear interface between the GaP and $Ga_xIn_{1-x}P$ is observed, which suggest a

compositionally graded interlayer formation. For heteroepitaxial $Ga_xIn_{1-x}P$ films on Si, a buffer layer of GaP is found to be necessary for optimum uniformity of the $Ga_xIn_{1-x}P$ layer. The selective growth of $Ga_xIn_{1-x}P$ on Si(001) is accessed.

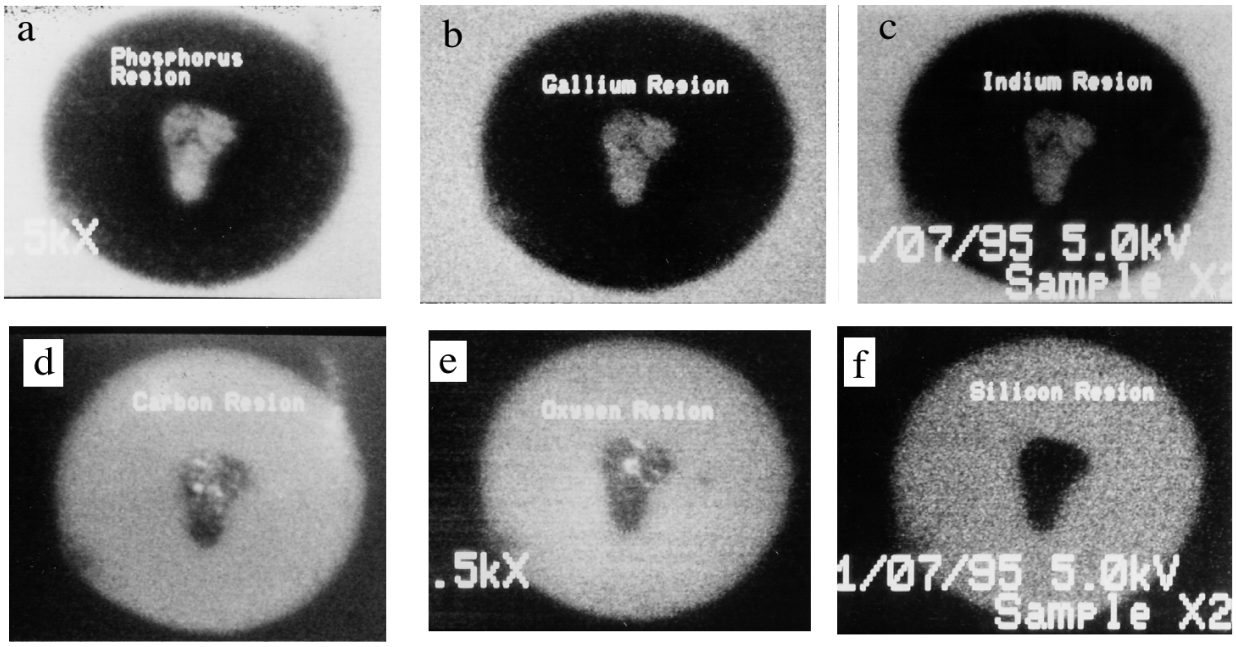


Figure 7: Semiquantitative micro analysis for Phosphorus, Gallium, Indium, Carbon, Oxygen anf Silicon at one of the holes shown in figure 6.

ACKNOWLEDGMENTS

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