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FERMI-LEVEL VARIATION ON GaAs(110) SURFACE WITH Sb OVERLAYER STUDIED WITH A PHOTOELECTRON MICROSCOPE*

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Abstract

Bare and Sb covered GaAs(110) surfaces were studied with a photoelectron microscope. For the cleaved surfaces, we observed maximum band bendings of 0.85 eV and 0.50 eV for *n*- and *p*-type GaAs respectively. For *n*-type, evaporation of Sb reduces the band bending from 0.85 eV to 0.55 eV. Annealing *p*-GaAs at 350 °C almost restored the flat band condition for an initially unpinned area. A reduction of band bending was observed for an initially heavily pinned area. This suggests that the cleavage defects originate partly from surface strain which can be removed by relaxing the strain with the formation of an ordered Sb overlayer. Sb desorbs from the GaAs surfaces when annealed at 560 °C. The Fermi level on this surface is at 0.35 eV above VBM regardless of initial band bending conditions. The new surface is attributed to the destructive process of Sb desorption.

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I. INTRODUCTION

GaAs (110) surfaces have been studied intensively in order to understand the mechanisms that cause Fermi-level pinning. In contrast to Si, the chemistry between GaAs(and other III-V's) and its native oxides did not lead to a chemically stable, defect free interface. Recently Sb/GaAs(110) system has attracted much interest because of its ordered and unreacted first monolayer(ML). Skeath *et al*[1] first observed that 1 ML of Sb adsorbed on GaAs(110) produced an ordered overlayer with the same symmetry as the underlying-clean GaAs substrate(110). Desorption experiments showed that the first ML is stable up to temperatures of ~400 °C and that Sb in excess of one ML desorbed at ~250 °C[2,16]. The surface structure determination by low energy electron diffraction(LEED) by Duke *et al*[3] shows that the Sb atoms are located in zig-zag sites which would be occupied by next epitaxial layer of GaAs. In a study of the Schottky barrier formation at the annealed Sb/*p*-GaAs interface, Schäffler *et al*[4] reported that annealing results in an interface with a high degree of perfection which is associated with a reduction of band bending from 0.6 eV to 0.28 eV. Recent experiments on *p*-GaAs by scanning tunneling microscope(STM) showed that no band gap states exists on regularly covered regions on GaAs[5]. However, in spite of intensive theoretical and experimental studies, the nature of band bending on Sb/GaAs interface is not yet clearly understood. Our experiments on the Sb/GaAs(110) have been carried out in part to study the effect of initial band bending conditions of cleaved surfaces on the band bending at Sb/GaAs(110) interfaces. For this purpose, experiments were performed on both initially pinned and unpinned surfaces using an UHV photoelectron microscope which has the spatial resolution of better than 10 μm[18].

As a continuation of the study on the correlation between the Fermi-level position and the surface topography we performed previously[10], we also studied cleaved GaAs(110) surfaces. In the previous work, it was shown that there is a good correlation between surface topography and the Fermi-level pinning positions. Also we reported that maximum band bending on GaAs(110) surfaces induced by bad cleavage resulted in a Fermi-level pinning position of 0.55 eV above

VBM for both *n*- and *p*-type[17]. But it was not known at that time whether metal such as Sb would cause the Fermi level on the surface pinned by cleavage defects(at 0.55 eV) to move to the Fermi-level position due to typical metal deposition(at 0.75 eV). An experiment on this subject was also performed in the course of experiments on Sb/GaAs(110).

II. EXPERIMENT

The instrument used in the experiment is a magnetic projection photoelectron microscope operating on a torroidal grating monochrometor(Beam Line 8-1) at the Stanford Synchrotron Radiation Laboratory. The photoelectron microscope is the magnetic analog of a field emission microscope. Photoelectrons emitted from a sample sitting in the high magnetic field(7T) from a superconducting solenoid are projected onto an imaging detector along the diverging magnetic field lines. A retarding field analyzer in front of the imaging detector allows for energy filtering of the image forming electrons. Design and operation of the microscope is described elsewhere[11,12]. The base pressure of the main chamber was better than $1x10^{-9}$ Torr. GaAs crystals were cleaved in situ from 5x5 mm bars of *n*-type ($7x10^{17}$ cm^{-3} Si doped) and *p*-type crystal ($1x10^{19}$ cm^{-3} Zn doped) obtained from Bertram Laboratories Inc, Somerville NJ. All the samples were outgassed by heating over 500 ^oC prior to cleaving. Sb was deposited using a resistively heated evaporator with the evaporation rate monitored by a quartz crystal thickness monitor. Subsequent anneals were performed at 350 ^oC in order to remove Sb in excess of 1 ML and achieve a single ordered monolayer. Finally the samples were annealed at 560 ^oC to remove Sb from the surface. Images were taken with various retarding potentials around the Ga 3*d* peak at $h\nu$ = 130 eV. Later, the topographies of the samples were studied by scanning electron microscope(SEM).

It is well known, in a semiconductor, that the binding energy of a surface core level varies with the band bending, where band bending is the difference between the surface and the bulk Fermi-level positions in the band gap. In regions of the surface with different degree's of band bending, we get core level electrons with different binding energies(or kinetic energies of photo-emitted electrons). This variation in kinetic energy of core level electrons results in image contrast. By setting the retarding potential in the microscope properly, for *p*-type, image contrast is generated such that the region with less band bending is bright(fewer core electrons are retarded since the kinetic energy is higher) while the region with more band bending is dark(more core electrons are retarded since the kinetic energy is lower). The case is reversed for *n*-type crystals where regions with more band bending will appear brighter. The intensity variation in a raw image is then transformed into a Fermi-level position map[10]. Here, a Fermi-level position map is a two dimensional display of the Fermi-level positions in the band gap.

Given the angle at which x-rays intercept the sample(15 degree off normal) and the nature of projection process, photoelectron microscopy of this form is largely insensitive to topology[18]. For bare surface, the image contrast is primarily derived from the band bending variation. However, there still exists image contrast derived from mechanisms other than variation in the band bending. Contributions may come from spatially non-uniform x-ray flux, topographic variations which cause effective x-ray flux variation on the sample surface, non-uniform overlayer coverages, or non-uniform background depending on the surface conditions. These factors are removed by normalizing the data image by the images taken at below the Ga 3*d* peak as well as one at above Ga 3*d* peak. This procedure ensures that we only count the contribution from band bending variation. The microscope operates with a retarding analyzer and so in practice the filtering is actually carried out on the integral spectra including a background of higher kinetic energy valence band electrons which are allowed to pass and participate in image formation. The photon energy of 130 eV was chosen such that the ratio of Ga 3*d* and valence band cross sections is large and the impact of valence band electrons(which only serves to reduce useful contrast) is small.

III. RESULTS AND DISCUSSION

A. *n*-type GaAs

Fig. 1 shows Fermi-level positions of an *n*-type sample as a function of the position across the crystal. This was made by aperturing and mechanical scanning technique[10]. Each point represents the Fermi-level position of a circular area with the diameter of 50 μm. The thin line shows the Fermi-level positions on bare surface. The Fermi-level position varies from 0.55 eV to 0.80 eV. It is interesting to notice that this maximum band bending is much larger than that induced by most metal depositions, which is typically 0.65 eV for *n*-type GaAs(Fermi level at 0.75 eV)[13]. After evaporation of 3 ML Sb(the thick line in Fig. 1), the whole area is pinned at 0.75 eV, including the area where the Fermi level was originally at 0.55 eV. Metal deposition, therefore, reduces the band bending on heavily pinned area so that the final pinning position matches that after metal deposition on the clean, defect free surface. These observations indicate that the natures of surface states, which cause the band bending, induced by cleavage defects and metal deposition are different.

Annealing Sb/*n*-GaAs at 350 °C did not show any significant reduction in the band bending. Essentially the Fermi-level positions remained the same as those without annealing. A number of experiments were performed on regions which were both originally pinned and unpinned and we did not observe any reduction in band bending. This appears consistent with earlier findings[6]. However, this does not agree with the theory which predicts that the Sb related surface states are close to valence and conduction band edges and should not lead to any significant band bending on *n*-GaAs as well as *p*-GaAs[14,15]. And recently two groups have reported observations of band bending reduction on Sb/*n*-GaAs[7,8,9]. It seems whether one can achieve band bending reduction on Sb/*n*-GaAs depends on the crystal quality as well as the preparation procedures. This poses sharp contrast to Sb/*p*-GaAs case, where one always finds that the near flat band condition is restored after thermal annealing. Careful and systematic studies need to be done in order to clarify this issue.

B. *p*-type GaAs

Fig. 2(a) shows Fermi-level position map of a *p*-type sample after cleaving. The maximum pinning position is at 0.5 eV. It is shown above that, for *n*-type GaAs, the maximum band bending due to cleavage defects is 0.85 eV(Fermi-level position at 0.55 eV). The Fermi-level position at ~0.5 eV is consistent with our previous results[10]. 0.5 eV above VBM is where the Fermi level lies, for both *n*- and *p*-type, with the maximum band bendings as a result of cleavage. But it remains to be answered whether there are surface states at this position. Evaporation of Sb on this surface pins the whole surface at 0.5 eV(Fig. 2(b)). For *p*-type GaAs, the observed maximum band bending by cleavage defects and that by metal deposition are very close so that it is not clear whether metal deposition actually reduces the band bending on the initially heavily pinned area.

We noticed that the Ga 3*d* signal from the initially heavily pinned area is more intense(sometimes it is twice as large) than that from the relatively less pinned area. Also the Sb 4*d* peaks were smaller on the originally heavily pinned area. These indicate that the heavily pinned area was not fully covered with Sb because of its roughness, hence we have a larger Ga 3*d* and smaller Sb 4*d* signals from this area.

Fig. 2(c) shows the Fermi-level position map after the sample was annealed at 350 °C. Band bending reduction is clearly seen the initially less pinned area where the Fermi level moved to 0.2 eV, which is consistent with other experimental results[4,6-8]. On the other hand the Fermi-level position on the originally heavily pinned area was not brought to the 0.2 eV position. Even though not fully, the band bending on heavily pinned area was also reduced. As stated in the above, there is a sign that this heavily pinned area was not fully covered with Sb(Ga 3*d* signal on this area was larger than that on less pinned area). We can see from the SEM picture of the same area(Fig. 2(e)) that this heavily pinned area contains many steps. With another *p*-type sample, we observed that the Fermi-level position of a region where the Fermi level was originally at 0.25 eV was brought to 0.20 eV upon annealing(This sample was uniformly covered with Sb considering that there was no variation in Ga 3*d* and Sb 4*d* signal intensities). So, the initially heavily pinned area may not have recovered to flat band condition because this area was not fully covered with Sb. And we believe that even this heavily pinned area can have near flat band condition once it is fully covered with Sb. Reduction of band bending on the initially pinned area upon annealing suggests that the surface states on cleaved surfaces are due to surface strain. Upon annealing the Sb/GaAs, not only does Sb bond to Ga and As atoms and brings the first layer of GaAs back to the bulk position[3,14] but it also relieves the surface strain that is present on the surface. This is not obvious if the initial band bending is comparable or smaller than the band bending after annealing. In that case, it is not clear whether the annealing of Sb/GaAs actually reduces the band bending due to cleavage.

Although the Sb desorption process has been studied[2,16], it has not yet been addressed how the Sb desorption process affects the GaAs surface. To study the effect of the Sb desorption processes on GaAs surfaces, the *p*-type sample was later annealed at 560 °C. All of the Sb on the surface has desorbed at this stage judging by the lack of Sb signal with $h\nu = 80$ eV. This agrees well with the result reported by Strümpler *et al*[16]. Fig. 2(d) shows the Fermi-level position map of the same area as Fig. 2(c) after the sample was annealed. The striking fact is that independent of the initial Fermi-level positions the Fermi-level positions after annealing at 560 °C were at 0.35 eV. That is, no spatial variation in Fermi-level position was observed. To see if this was due to a pure annealing effect rather than due to the Sb desorption effect, we also annealed a bare GaAs surface with spatial variation in pinning position at the same temperature. The result(not shown here) shows no change in band bending and the spatial variation of Fermi-level position remains same up to 560 °C. Hence Fermi-level pinning at 0.35 eV was not due to an annealing effect. Rather the Sb desorption process is responsible for the new surface which has no variation in the Fermi-level position. If the desorption process were not destructive, the Fermi-level positions should be restored to where they used to be. In that case Fig. 2(d) should be similar to either Fig. 2(a) or Fig. 2(c). So we attribute this new surface to destructive desorption process of Sb. It is likely that Sb desorbs with Ga or As. Experiments with high resolution photoemission spectroscopy should be carried out to confirm this.

V. CONCLUSION

Our studies on band bending behavior on bare and Sb covered GaAs(110) surfaces lead to the following conclusions:

(i) The Fermi-level positions of the maximum band bending due to cleavage defects are at ~0.5 eV for both *n*- and *p*-type. The nature of the surface states induced by cleavage is different from that due to metal deposition.

(ii) Cleavage defects originate from surface strain and these can be removed by forming an ordered monolayer of Sb and relaxing this surface strain.

(iii) Sb desorption is a destructive process. Sb may desorb with Ga and As, and the resulting surface, for p-type GaAs, has Fermi-level position at 0.35 eV.

Even though few things remain to be answered, our experimental results give a consistent picture on cleaved and Sb covered GaAs(110) surfaces. Additional experiments with the microscope and other techniques need to be performed to answer the remaining questions.

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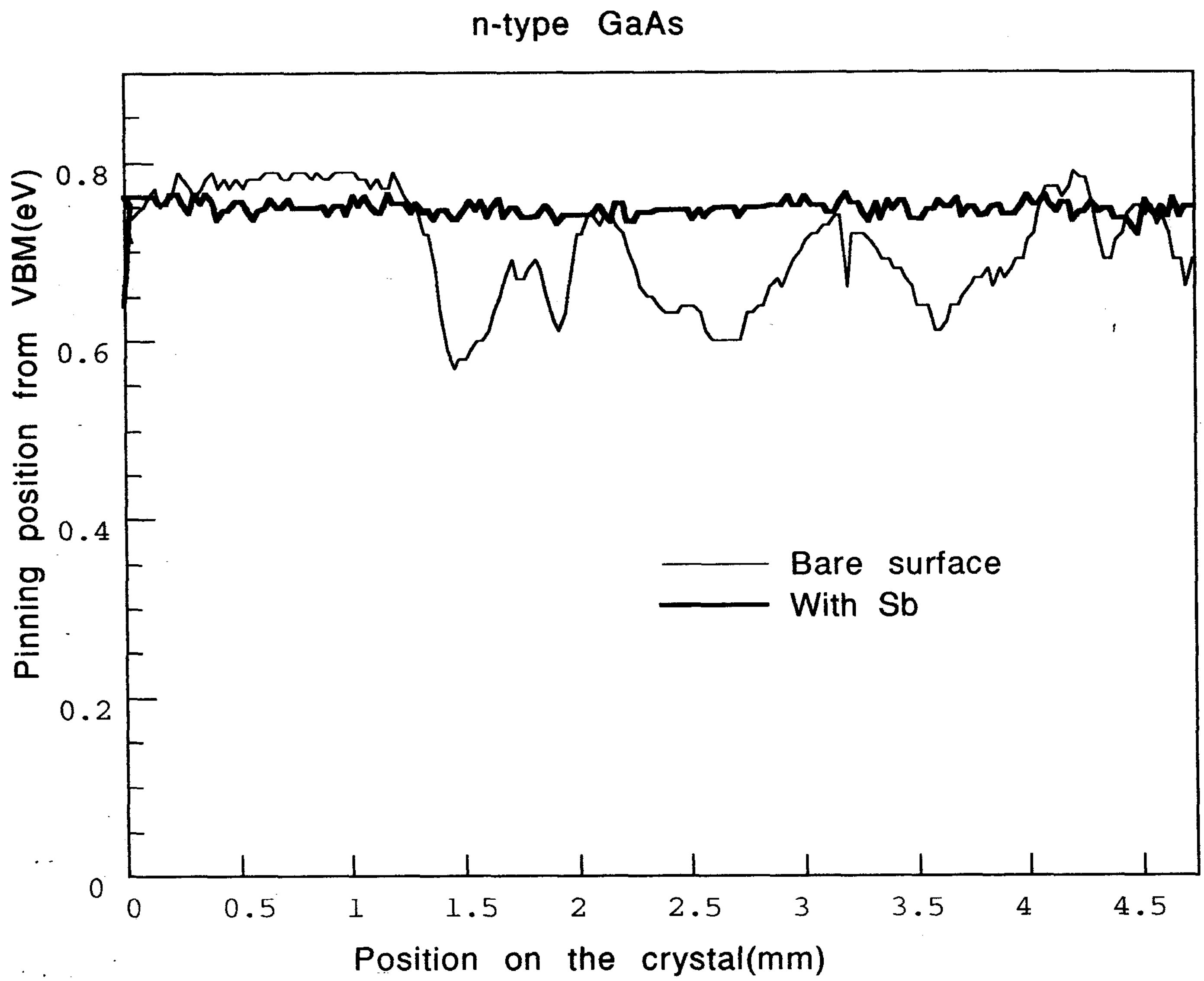
microscopy, see Chap. 1.

Fig. 1. The surface Fermi-level position from the VBM on an *n*-type GaAs(110) as a function of position across the crystal. The thin line shows the surface Fermi-level position on the bare surface and the thick line shows the surface Fermi-level position after evaporation of 3 ML Sb.

Fig. 2. (a) The Fermi-level position map of *p*-type GaAs on the bare surface. The gray scale shows the surface Fermi-level position with respect to the VBM. The maximum pinning is at 0.5 eV. (b) The Fermi-level position map after evaporation of 3M Sb. (c) After annealing at 350 °C. (d) After annealing at 560 °C. (e) SEM micrograph of the same area.



n-type GaAs
Pinning position from VBM(eV)
0.8
0.6
0.4
0.2
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Position on the crystal(mm)
Bare surface
With Sb

Fig 1

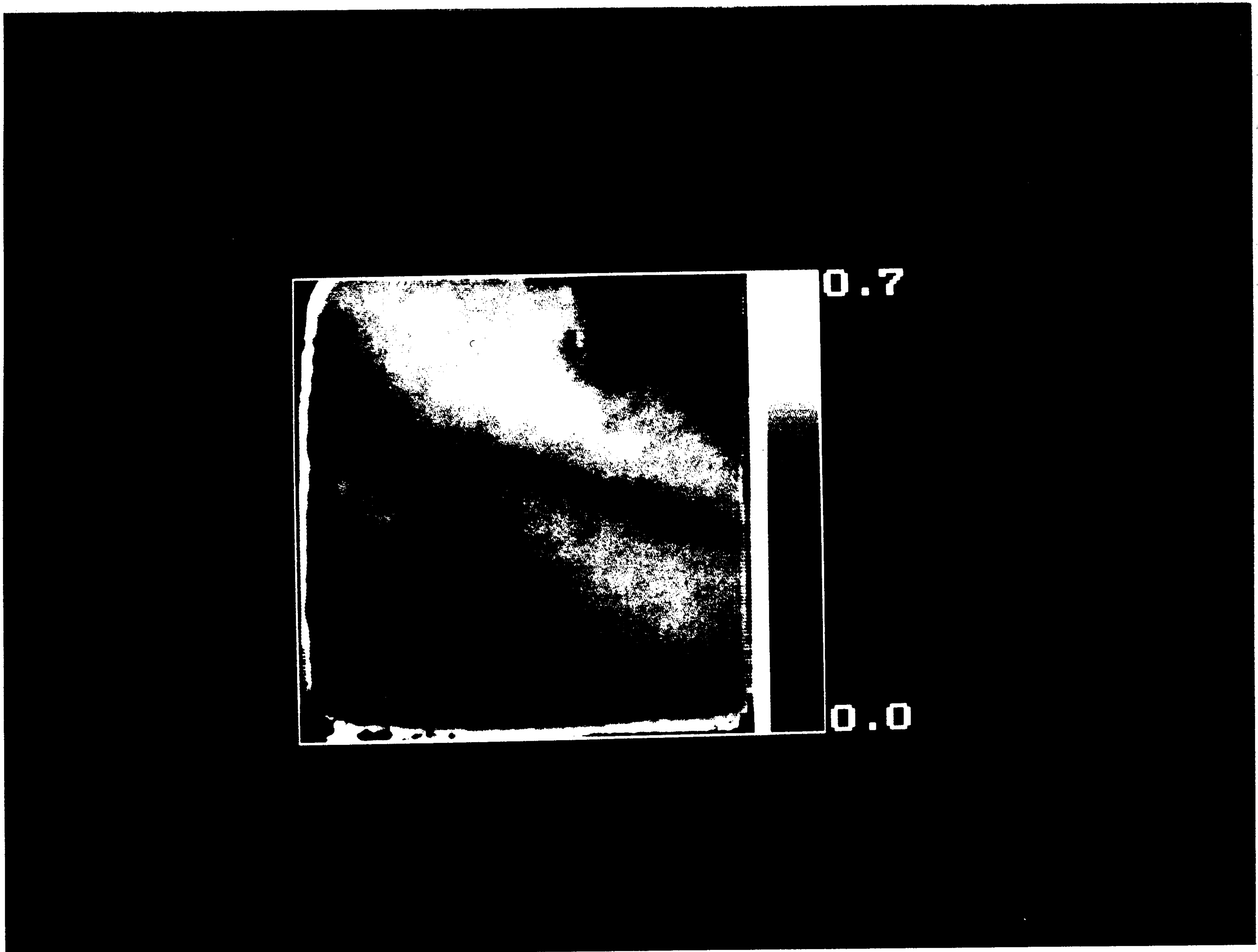


Fig 2.a

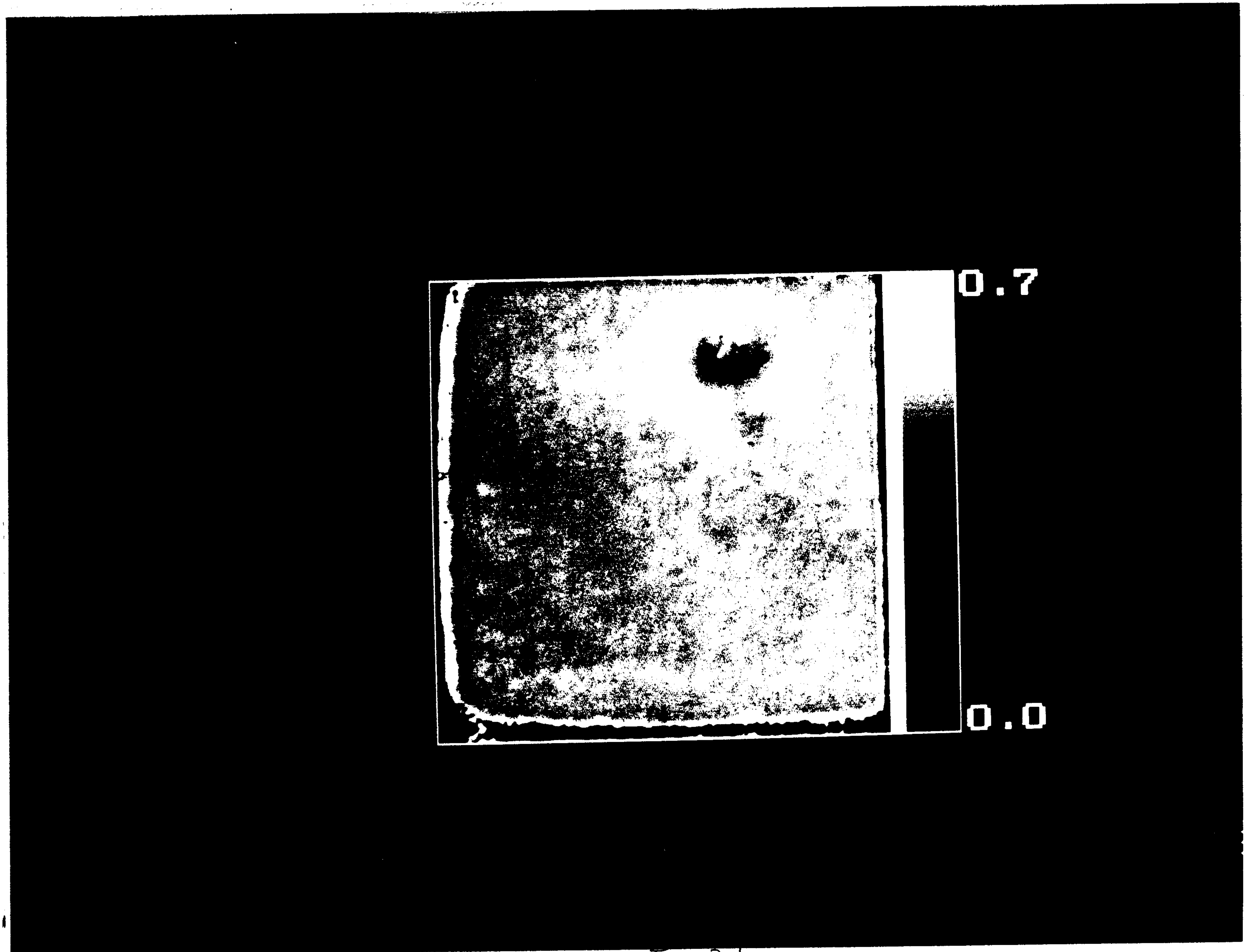


Fig 2.6

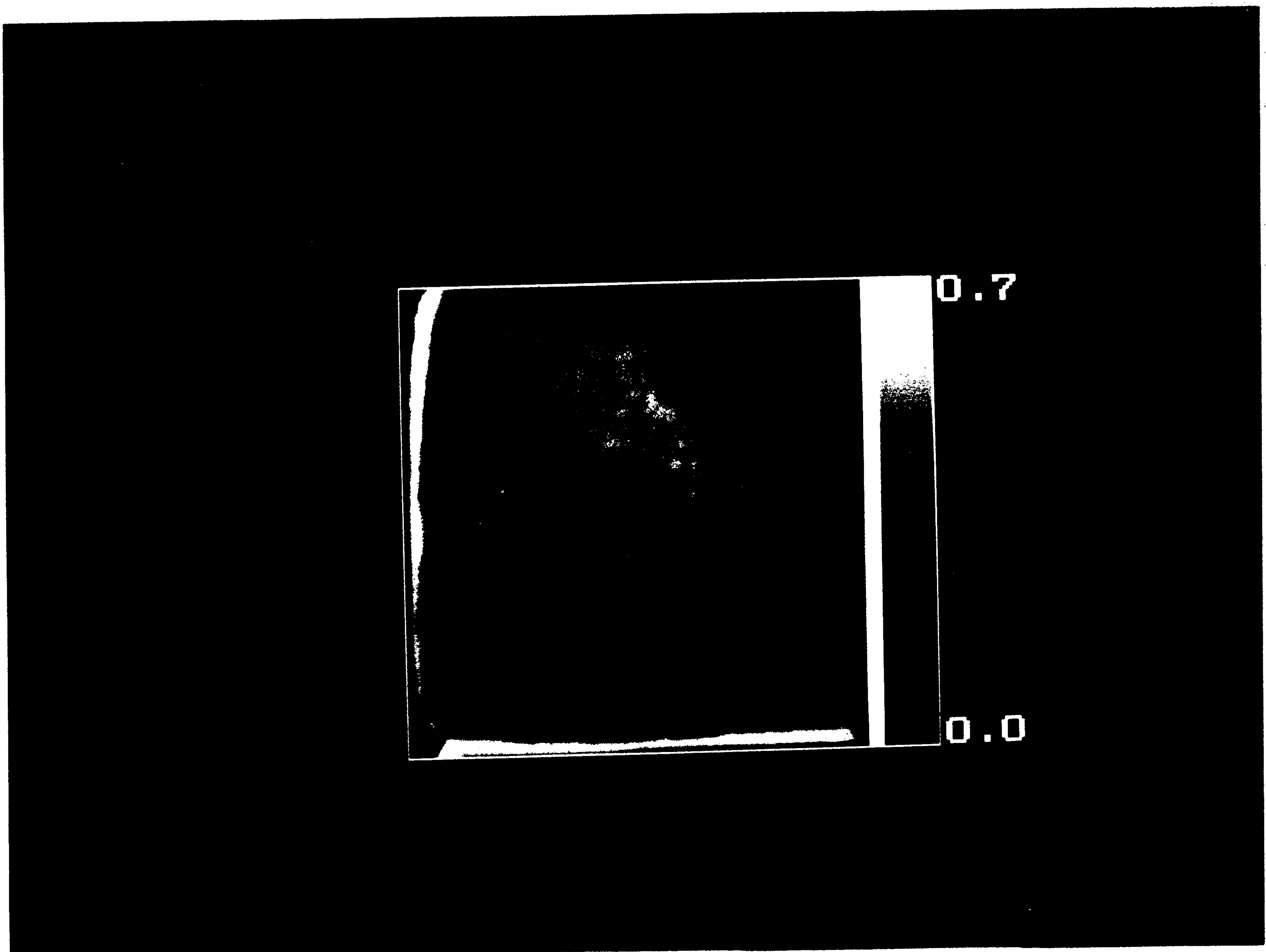


Fig 2.C

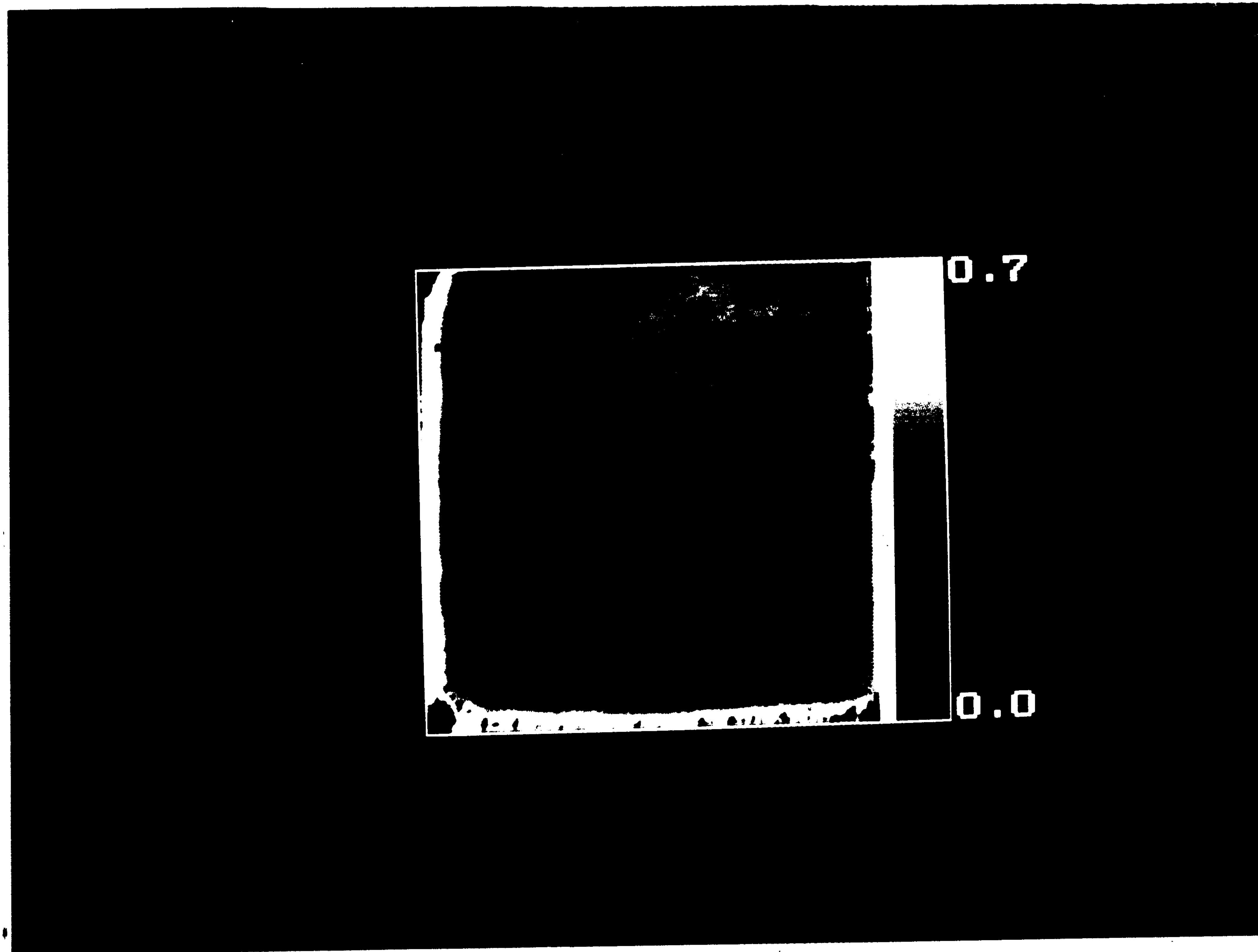


Fig 2.d

Fig 2.e