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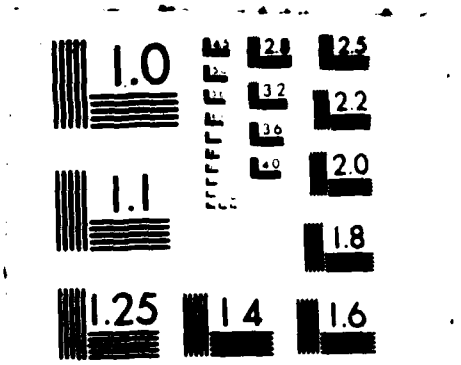

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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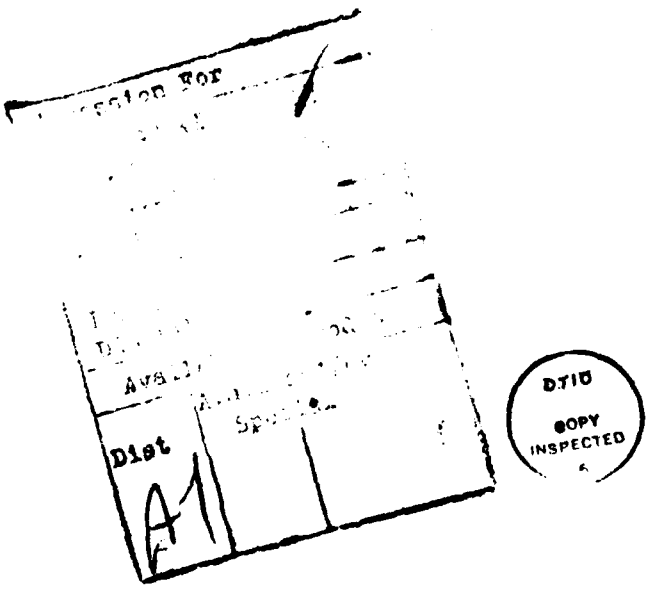

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Unpinning of the Fermi level on GaAs (100) surfaces by photochemical reactions resulting from simultaneous exposure of specimens to flowing water and light was recently reported. ~~We discuss here~~ a series of experiments carried out to provide further information on the changes in surface electronic structure responsible for unpinning of the Fermi level under these conditions. The present work supports the conclusion that the surface states which pin the Fermi level are associated with elemental arsenic and arsenic sesquioxide.

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19. KEY WORDS (Continued)

20. ABSTRACT (Continued)

(As_2O_3). Effects of each of these two species on pinning are distinguished experimentally. ~~We find that,~~ in addition to photochemical reactions, exposure to flowing water alone can result in Fermi level unpinning under certain conditions. The oxygen content of the wash water and the specimen preparation are shown to be important variables.

UNPINNING OF THE FERMI LEVEL ON GaAs BY FLOWING WATER

The Fermi level on GaAs (100) surfaces has been unpinned by exposure of specimens to flowing water and light.[1] We describe experiments in which we demonstrate unpinning of the surface Fermi level on n-type GaAs (100) surfaces both photochemically and by exposure to flowing water in the absence of light.

The Fermi level on GaAs is "pinned" by charge trapped in surface states. It has been proposed that the electronic states responsible for Fermi level pinning are associated with metallic arsenic (As^0) and As_2O_3, and that unpinning can be explained by the chemistry of these species in water.[1] As_2O_3 is readily soluble in water.[2] Although insoluble in water free of dissolved oxygen, As^0 is oxidized to soluble As^{+3} in water containing dissolved oxygen.[2] In addition, As^0 can also be oxidized photochemically to a soluble species by holes generated by incident light. We have investigated the effects of two important factors, sample surface preparation and oxygen concentration in the wash water, on Fermi level unpinning. Our results give further insight into the unpinning mechanism, and in particular help elucidate the roles of both As^0 and As_2O_3 in Fermi level pinning.

The samples were n-type silicon-doped GaAs (100) (1 to 5 X $10^{17}/cm^3$) and were polished by the manufacturer (Morgan Semiconductor, Inc.). The samples were either used "as received" (after a standard degreasing process) or were etched with H_2SO_4/H_2O (1:1 by volume) for 5 minutes.

On "as-received" GaAs, the native surface oxide is a mixture of Ga_2O_3 and As_2O_3, with a relatively small amount of As^0.[3] On etched material, most of the bulk oxide is removed, and the surface concentration of As^0 is increased.[4] The surface Fermi level was found to be pinned on both as-received and etched GaAs.

We used photoluminescence (PL) as an indicator of Fermi level unpinning.[1] As the Fermi level unpins, the band bending, and the associated electric field, decrease. Photoelectrically generated electron hole pairs thus are more likely to recombine radiatively before being separated by the field, and the PL intensity is enhanced accordingly.

Samples were "unpinned," as evidenced by increased PL intensity, simply by washing them in a stream from the laboratory deionized (DI) water tap (oxygen concentration: 5 ppm) while exposing them to the light from a 150 W microscope illuminator. Under these conditions, we found that the Fermi level was unpinned only by simultaneous exposure of specimens to water and light, in agreement with the results of ref. 1.

In this report, we present the results of experiments conducted to study the effects of deoxygenated and oxygen saturated water on "as-received" and acid etched GaAs. In order to carry out these experiments under controlled conditions, an apparatus which provides both for sample washing and drying and PL measurement was constructed. Samples were mounted on a spinning chuck. A stream of DI (18 megohm-cm) water, fed from a glass reservoir pressurized by a gas (nitrogen or oxygen) bubbler, was directed onto the sample through a syringe. The reservoir is either pressurized by oxygen, which saturates the water with oxygen (41 ppm at 25°C), or with nitrogen, which reduces the oxygen content of the water to a very low level ($\leq$ 0.1 ppm). The samples were then dried by spinning them in a stream of nitrogen or air. These jets of gas could be heated. After drying, PL measurements were made using a chopped 15 mW helium-neon laser (632.8 nm) as an excitation source. The HeNe laser was focused through a 10X microscope objective to an approximately 2 mm spot on the sample surface for PL excitation. A 100 W quartz-halogen lamp can also be focused through the objective to the same spot to stimulate photochemical reactions. The bandgap PL radiation from the specimens at 860 nm was synchronously detected after passing through an Oriel one-eighth meter grating monochromator. An optical filter (Schott RG 695) eliminated stray exciting light.

We first describe the results of the experiments in which the wash water was thoroughly deoxygenated by bubbling nitrogen. As-received samples initially washed in the dark showed a factor of 2 increase in the PL intensity over the PL signal level before unpinning (background). Some reduction of surface state density and an associated PL intensity increase would be expected just by washing as-received material in deoxygenated water as the dominant As_2O_3 is removed. After more washing with the tungsten lamp on,

samples showed a further increase in PL intensity over the enhancement observed without illumination, to about a factor of 3 over the background. Photochemical reactions lead to only a modest additional PL increase because As^0 is not a major surface constituent, and a photochemical reaction is therefore not required for a significant increase in PL to occur. Samples pretreated by washing in the H_2SO_4/H_2O etch, followed by deoxygenated water rinse and nitrogen drying, showed at best only a slight enhancement of the PL intensity without illumination. Washing these samples while illuminated by the quartz-halogen lamp produced a substantial increase in PL intensity, typically by a factor of 3. These observations are both explained if As^0, insoluble in oxygen-free water but oxidizable photochemically, is the dominant surface species. We also observed that, once unpinned, the PL intensity after decay can be increased to its original value by water washing alone. This observation implies that the surface repins by interaction with atmospheric oxygen to form a soluble species, such as As_2O_3, which can be removed easily by further washing.

The time dependence of the PL intensity when samples unpinned by flowing deoxygenated water were exposed to a stream of heated air or to heated nitrogen is also consistent with the arsenic/arsenic oxide model. With heated air exposure, a PL decay with a pronounced temperature dependence is seen, while the PL intensity decays much more slowly in the stream of heated nitrogen (Fig. 1). The surface thus "repins" when the GaAs is oxidized in air.

The PL intensity is also increased by alternating cycles of specimen heating and washing with deoxygenated water. After an initial washing, the PL intensity of an as-received sample increased by a factor of 2. The sample surface was then exposed for 15 seconds to 170°C air, which caused the PL signal to decay to its initial intensity. This procedure was repeated three times, with signal enhancement noted over each cycle, after which a maximum intensity was reached. Heating apparently converts any residual insoluble As^0 to soluble As_2O_3, which then washes away. Each cycle thus leads to an increase in PL intensity until all of the As^0 that is initially on the surface is oxidized and removed.

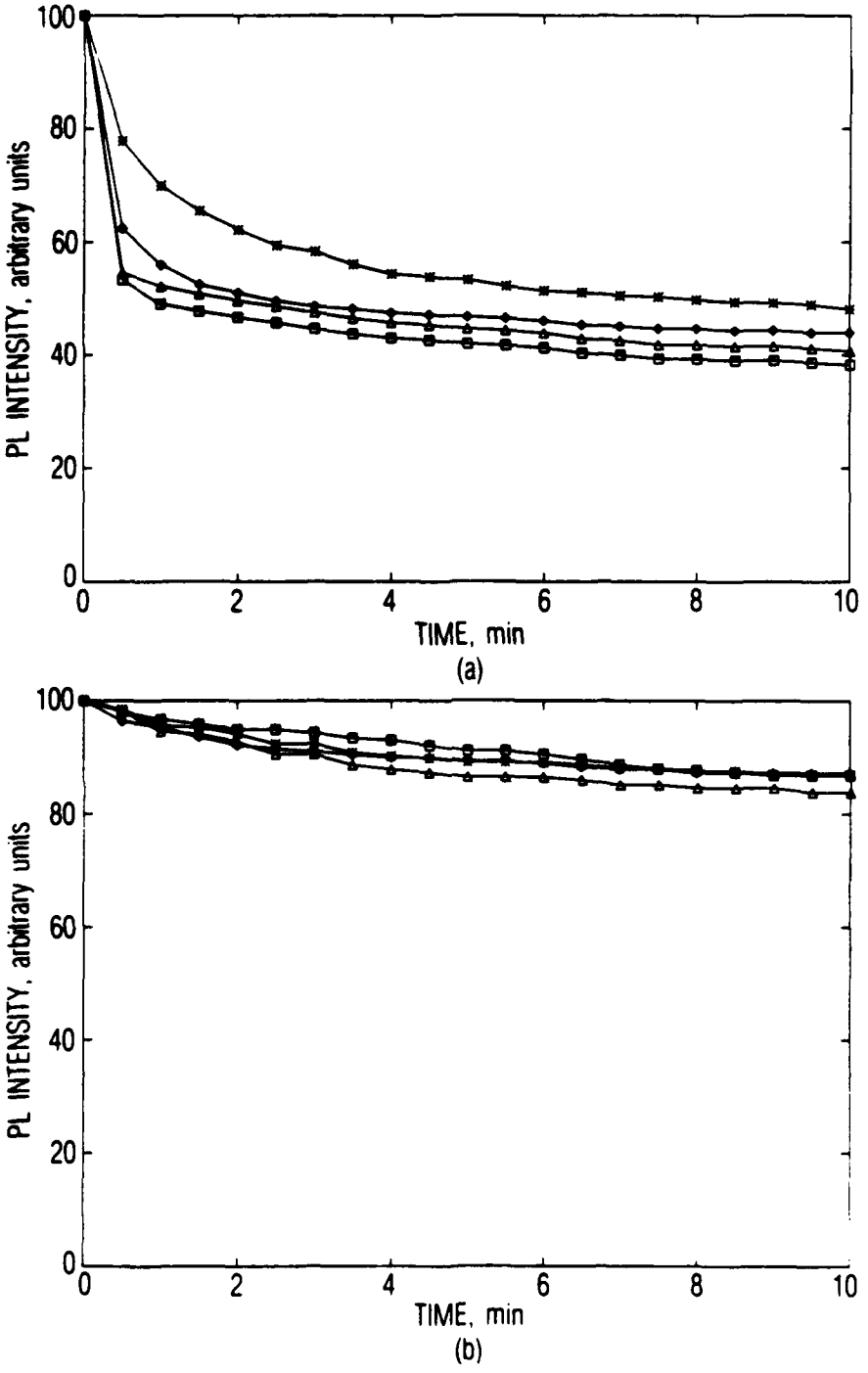

Fig. 1. PL Intensity vs. Time (Arbitrary Units, Data Normalized to 100 at Time Zero). Asterisk - 23°C; diamond - 50°C; triangle - 100°C; square - 150°C. (a) Specimens in heated air; (b) specimens in heated nitrogen.

In contrast to deoxygenated water, in which As^0 is insoluble, both As_2O_3 and As^0 are soluble in oxygenated water. In the next series of experiments, we studied the effects of water saturated with oxygen on as-received and acid etched specimens. The PL intensities as a function of the cumulative time of washing for an as-received specimen washed in oxygen saturated water and, for comparison, an as-received specimen washed in deoxygenated water, are shown in Fig. 2. These data were obtained by alternately washing specimens for various times, then drying them and measuring their PL intensities. The PL intensity decays with time, and the data represent the maximum intensity attained after each washing. With oxygen saturated water, the PL intensity reached a maximum at about 2 minutes, then dropped rapidly. With deoxygenated water, the PL intensity reached a maximum and did not decrease appreciably with further washing.

In deoxygenated water, as-received material is unpinned, at least partially, when the predominant arsenic species, As_2O_3, is dissolved. Some residual As^0 may remain on the surface, but no new oxidized arsenic species can form. Figure 2 suggests that, when as-received GaAs is washed with oxygen saturated water, As_2O_3 goes into solution while As^0 is first oxidized, then also goes into solution. The removal of these two arsenic species from the surface leads initially to an increase in the PL intensity, even above the level recorded for washing in deoxygenated water. However, we believe that after a few minutes of washing a surface oxide layer, largely Ga_2O_3, is formed on GaAs. This insoluble oxide layer interferes with oxygen transport to the GaAs substrate and with the transport of As^{+3} away from the substrate. As_2O_3 may thus be stable, or at least in dynamic equilibrium, at the interface, and the surface cannot be maintained in an unpinned condition. It has been reported that GaAs surface oxides may be removed by flowing water under some conditions.[5] Our data, however, are better explained by the formation of a passivating oxide layer as suggested in ref. 1. We have found that surfaces, once exposed to prolonged washing in oxygenated water without light, cannot be unpinned by washing with oxygenated water while illuminated. This observation is consistent with the hypothesis of a passivating oxide layer. The photochemical unpinning process requires the access of chemical species to and from the

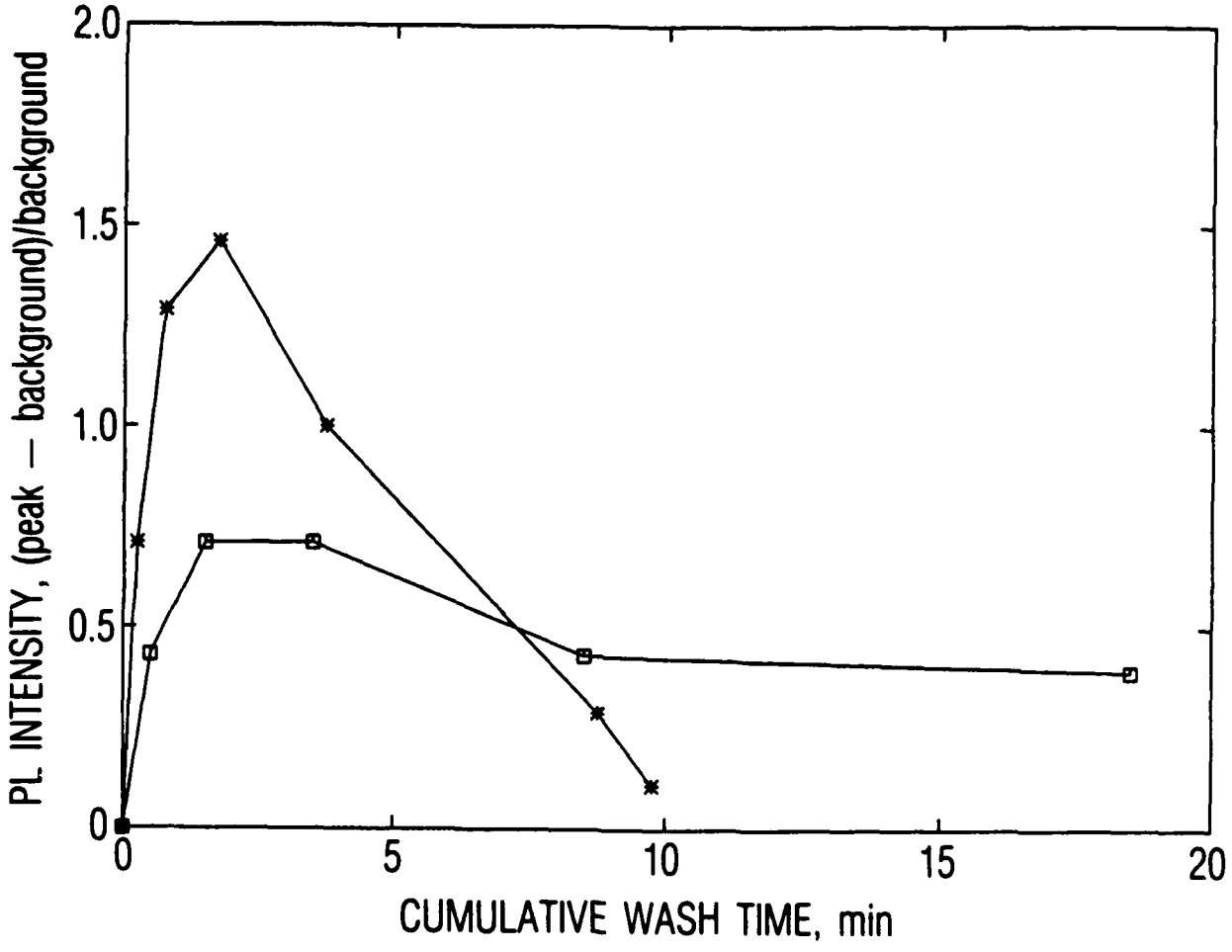

Fig 2. PL Intensity vs. Cumulative Washing Time for As-Received Specimens Exposed to Successive Washings with Oxygen Saturated Water (Asterisks) and Deoxygenated Water (Squares). The PL intensity begins to decay toward background after each wash. Data that represent the maximum PL intensities attained after each washing are plotted.

surface. Photochemical unpinning is impeded when surface access is blocked by an oxide layer.

Additional experimentation is essential for complete understanding of the surface chemistry of Fermi level unpinning, but we have presented a consistent explanation of our observations. In addition to unpinning by washing in the presence of light, we have demonstrated that the Fermi level on n-type GaAs may be unpinned by the action of flowing water alone.

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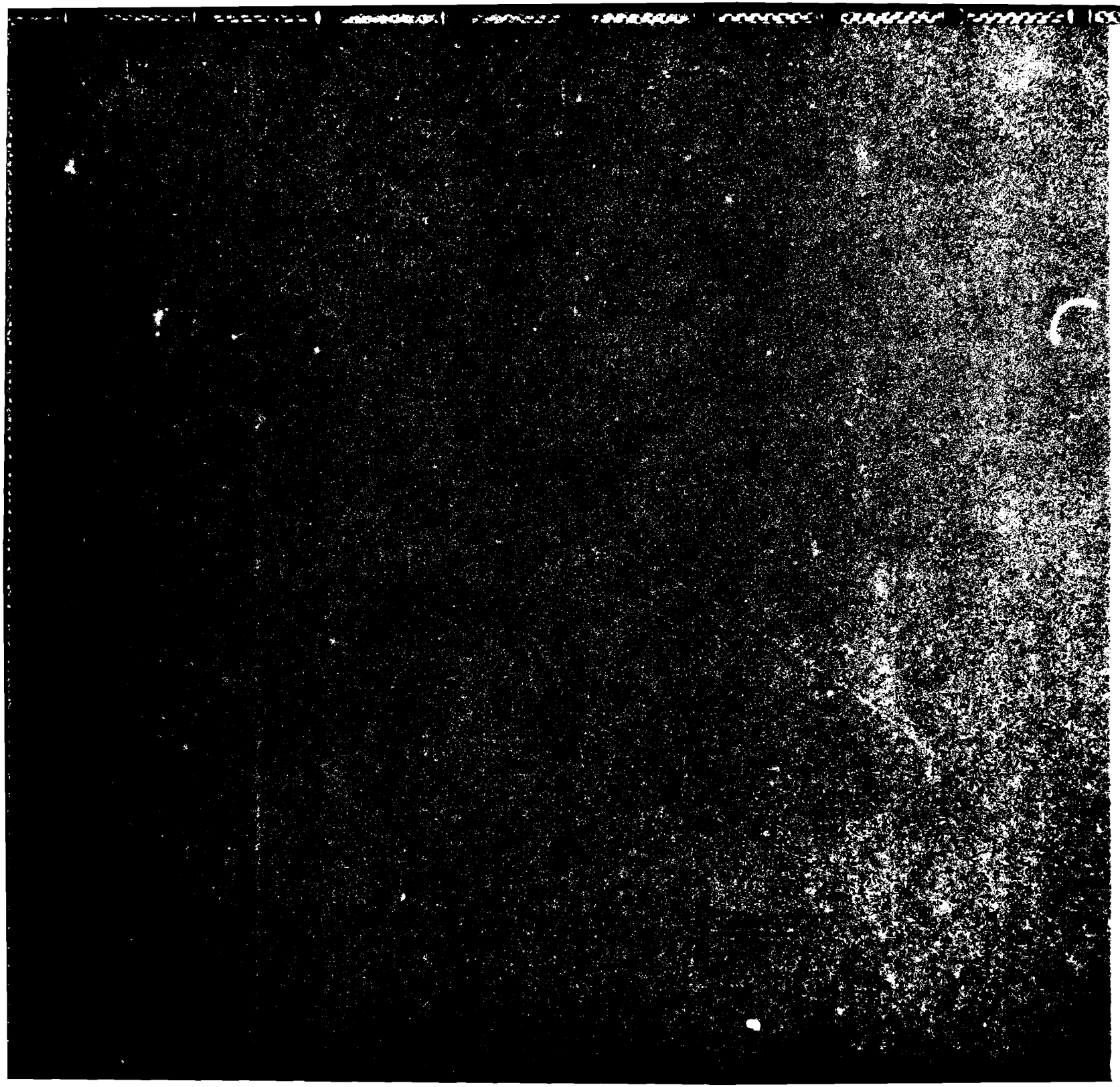

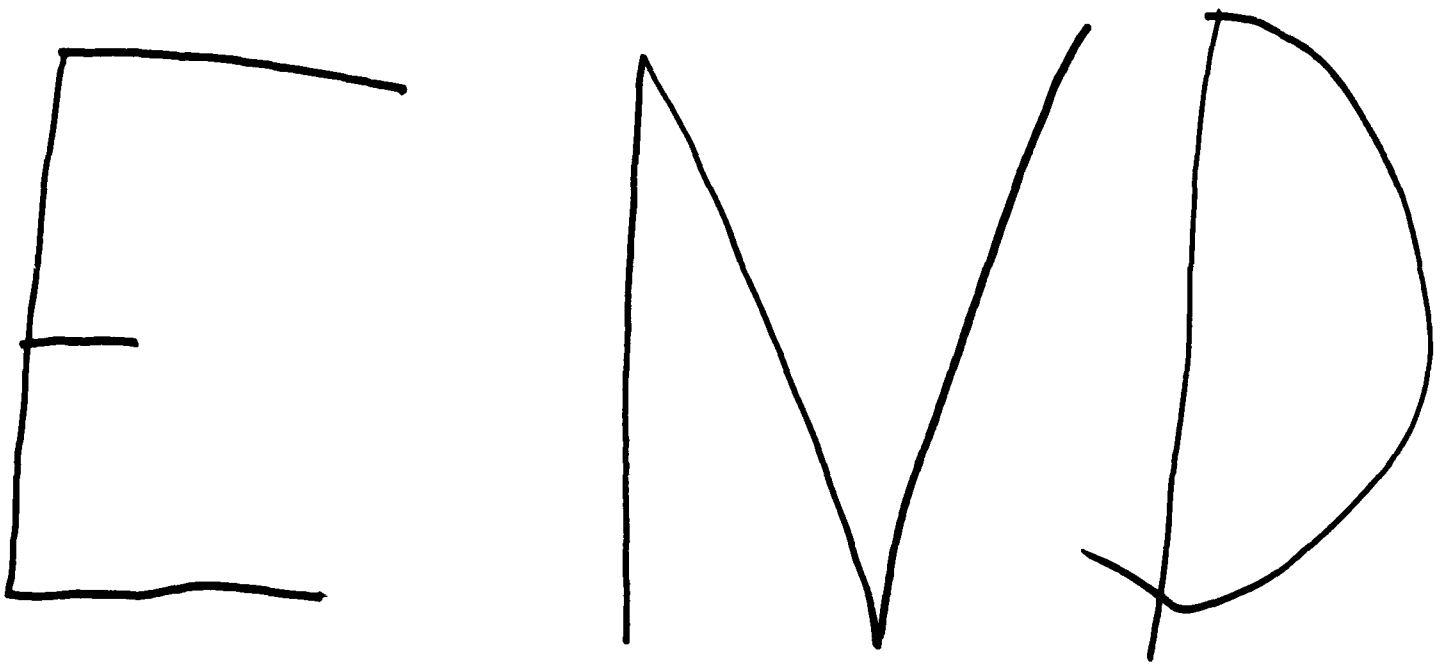
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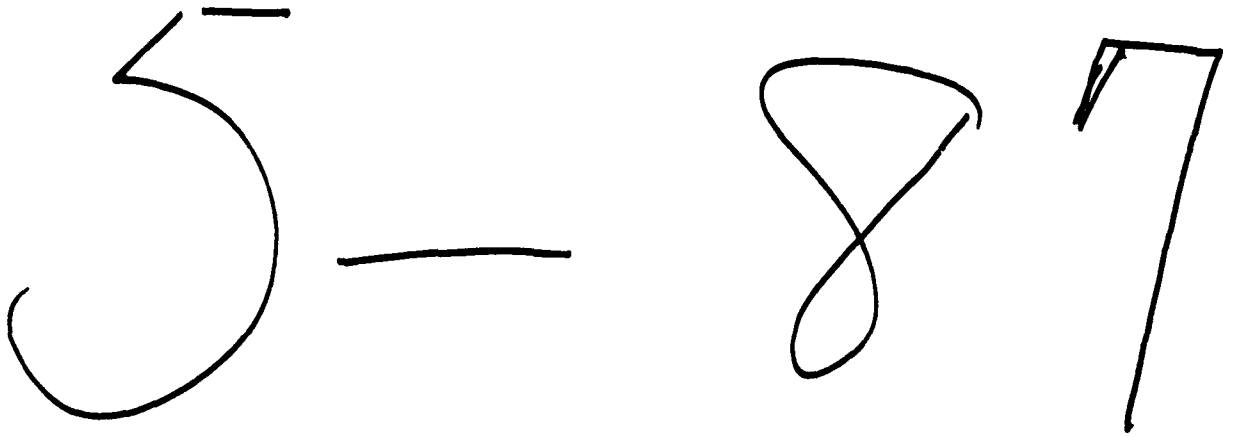
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