Surface analysis of reactive ion-etched InP

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A dry-etch process for InP is developed using a mixture of Cl_2, Ar, CH_4, and H_2. This process results in a high etch rate and good anisotropy. The induced damage is investigated by surface characterization after etching, using x-ray photoelectron spectroscopy, Rutherford backscattering spectrometry, photoluminescence measurements, and transmission electron microscopy. The etch mechanism is briefly discussed.

It is becoming increasingly clear that dry-etching techniques will play an important role in the fabrication of III-V devices because of the ongoing reduction of structure dimensions.[1]

A common objection against dry etching is that it may cause damage in the etched material. Damage can consist of structural or compositional changes, deposition of material on the surface, and diffusion into the substrate. Some reports state that damage can be found at depths of well over 10 nm in the material.[2–7]

An investigation of the damage, especially surface damage, caused by a chlorine-based etch process for InP by a range of sensitive analysis techniques is reported here: scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectroscopy (RBS) photoluminescence intensity measurements (PLI), and transmission electron microscopy (TEM). The etch mechanism is also briefly discussed.

At this moment a large diversity of techniques for dry etching is available, such as sputter etching, reactive-ion etching (RIE), electron cyclotron resonance (ECR) RIE, ion-beam etching (IBE), and chemically assisted IBE (CAIBE). Some of the gases used are He, Ar, Xe, Cl_2, CCl_4,CF_4, CH_4, and H_2. Several authors[8–10] have proposed that RIE of InP usingCH_4/H_2 instead of chlorine-containing mixtures should lead to less damage, but this has not always been confirmed.[11] Currently much attention is paid to etching with low ion energies, to preclude structural and/or compositional changes of the material caused by the impact of ions. Low ion energy, of the order of 100 eV, is achieved using magnetically enhanced RIE (MERIE) and ECR RIE.[12,13] Some authors have reported effects at depths up to 0.3 μm.[2–7] It is the purpose of this work to demonstrate that anisotropic etching of InP can be performed using a Cl_2-based RIE process, with so little damage as to be acceptable for device fabrication.

RIE, with Cl_2 as the main etchant species,was carried out in an Alcatel GIR300 RIE apparatus. This is a 15-cm-diam electrode parallel-plate machine, with the lower electrode powered at 13.56 MHz. The gases used are Cl_2, Ar, CH_4, and H_2, with flows of 4, 4, 4, and 24 sccm, respectively, and the pressure is 2.5 Pa. The quartz substrate holder is placed on the lower electrode, and is heated to 200 °C. The applied total powers are 100 and 200 W, or 0.5 and 1.0 W/cm^2 corresponding to bias voltages of 480 and 770 V, respectively. The sample surface has a temperature of approximately 215 and 240 °C respectively.

The InP substrate material used is cleaned by etching in H_2SO_4:H_2O_2(5:1) and H_2SO_4 to remove surface contamination and oxides prior to RIE. The sample area is 2–4 cm^2. The process gives a smooth etched surface and is highly anisotropic, as can be seen from the SEM micrograph (Fig. 1). The etch rate is 0.3 μm/min for both 0.5 and 1.0 W/cm^2. It was applied successfully for the etching of laser mirrors.[14] In all of the following results the surface composition was found to be homogeneous on a sample and reproducable.

An elevated temperature is necessary to evaporate the $InCl_x$ etch products. At lower temperature $InCl_x$ will remain on the surface and the surface becomes rough.[15] We have confirmed the presence of $InCl_x$ on these rough surfaces by Auger electron spectroscopy.

First the chemical composition of the surface after RIE is determined. XPS is especially sensitive to surface contamination. XPS is performed under 90° and 20° electron takeoff angles, with the latter giving more information about the near-surface region. The P/In ratio of the etched samples is very different from that of the unetched reference sample, as can be seen in Table I. Apparently the surface becomes enriched in P by RIE, and this effect increases with applied power, especially in the near-surface region detected by XPS under 20° electron takeoff angle (typically 1–1.5 nm).

Transfer of the samples from the etching apparatus to the XPS analysis was done under continuous nitrogen flow to prevent oxidation of the surface by air. As a result only a little oxygen can be seen in the etched samples, but the 1-nm top layer contains a substantial quantity of carbon. Since this is not due to deposition from air the carbon must have been deposited by the RIE etching process.

XPS is capable of detecting the gases Cl_2 and Ar to below 1% atomic concentration in the top layer, so it is assumed that little Ar or Cl penetrates into the substrate or remains chemically bonded to it. Auger electron spectroscopy has also been applied, yielding the same result.

RBS, with 2-MeV He^+ and a detection angle of 170°, has been used to study structural changes in the near-surface region. Channeling along the ⟨100⟩ axis has been ap-

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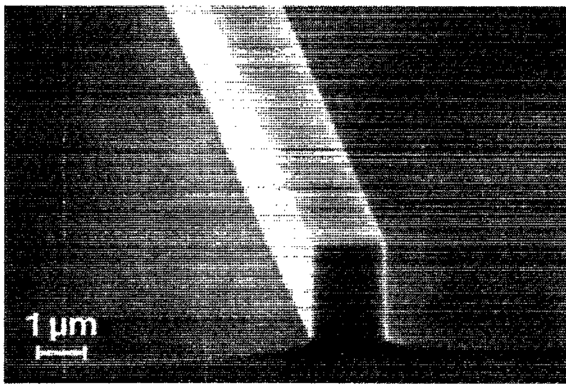

FIG. 1. SEM micrograph of a mesa and the smooth-etched surface in InP.

plied, so an increase of the yield of the In surface peak indicates an amorphous top layer. In Fig. 2 we show the result for the reference sample and the samples etched at 0.5 and 1.0 W/cm^2. No increase or broadening in back backscattering yield of the In surface peak was detected which implies an upper limit of approximately 4×10^{15} cm^{-2} displaced In atoms in the top 15 nm. The number of In atoms in a monolayer of InP is 7×10^{14} cm^{-2}.

High-resolution TEM micrographs of the surface, shown in Fig. 3, reveal that the surface of all substrates is covered with an amorphous layer, in apparent contradiction with the RBS results. This will be discussed below. The thickness of the layer increases with applied power. For the sample etched at 0.5 W/cm^2 it is 2.2 nm and at 1.0 W/cm^2 it is 4.5 nm. The interface of the sample etched at 1.0 W/cm^2 is less smooth than that of the reference sample and the sample etched at 0.5 W/cm^2.

TABLE I. P/In ratio of the surface of an unetched reference sample, a sample etched at 0.5 W/cm^2, and a sample etched at 1.0 W/cm^2 according to XPS. Measurements are performed under 20° and 90° electron takeoff angles, yielding information about surface layers with a typical thickness of 1–1.5 nm and 3–4 nm, respectively.

Sample	Reference	0.5 W/cm^2	1.0W/cm^2
20°	0.61	2.1	2.8
90°	0.74	1.3	1.4

Combining the data of the TEM micrographs with those of the surface analysis it is possible to evaluate the composition of the amorphous layer. From the XPS data it seems that the layer consists mainly of phosphorus and only the topmost 1.5 nm is rich in carbon. The amount of carbon is independent of power.

There seems to be a contradiction between the amorphous layer revealed by TEM and the ion-channeling results, which allow only a 2-nm layer of disordered material. This can be resolved by taking into account the composition of the top layer. According to the XPS analysis the amorphous layer of the 1.0-W/cm^2 sample contains little In to 4.0-nm depth. Since it is In and not P to which RBS is most sensitive, the TEM result is not inconsistent with the ion-channeling results. Note that in the case of CH_4/H_2 etching, the near-surface region will be enriched in In, yielding a different channeling RBS spectrum.[11]

The above results, especially TEM, seem to indicate that the damage of the surface after RIE is all concentrated in the amorphous top layer. This is confirmed by PLI measurements. Although it is difficult to extract quantitative results from PLI measurements[16] we know that they are

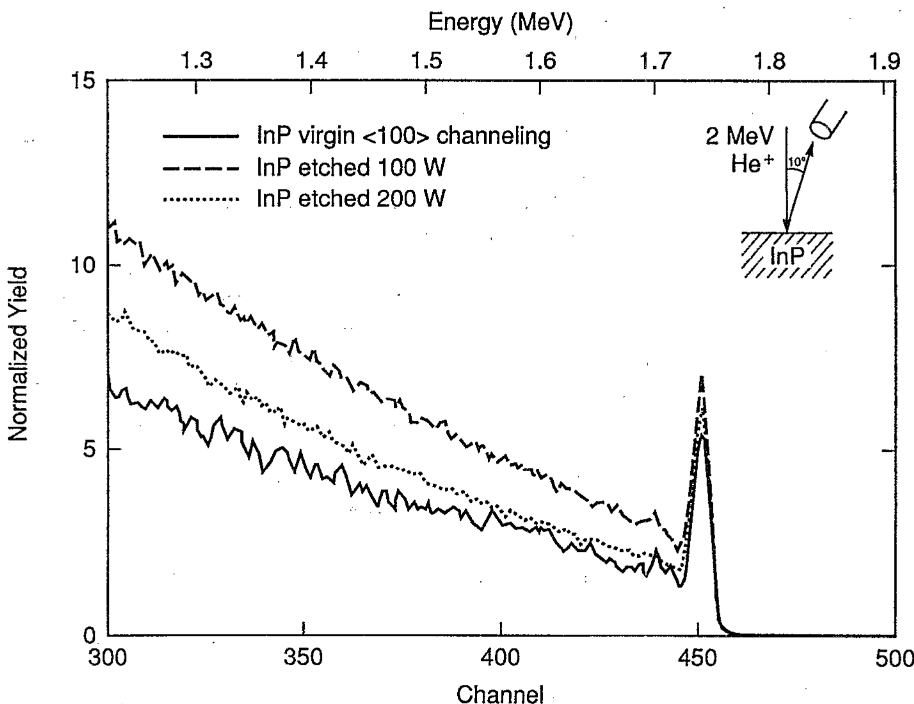

FIG. 2. Channeling RBS spectra with the ion beam aligned to the InP ⟨100⟩ axis, as shown in the inset. The In surface peak is not broadened after RIE at 0.5 or 1.0 W/cm^2.

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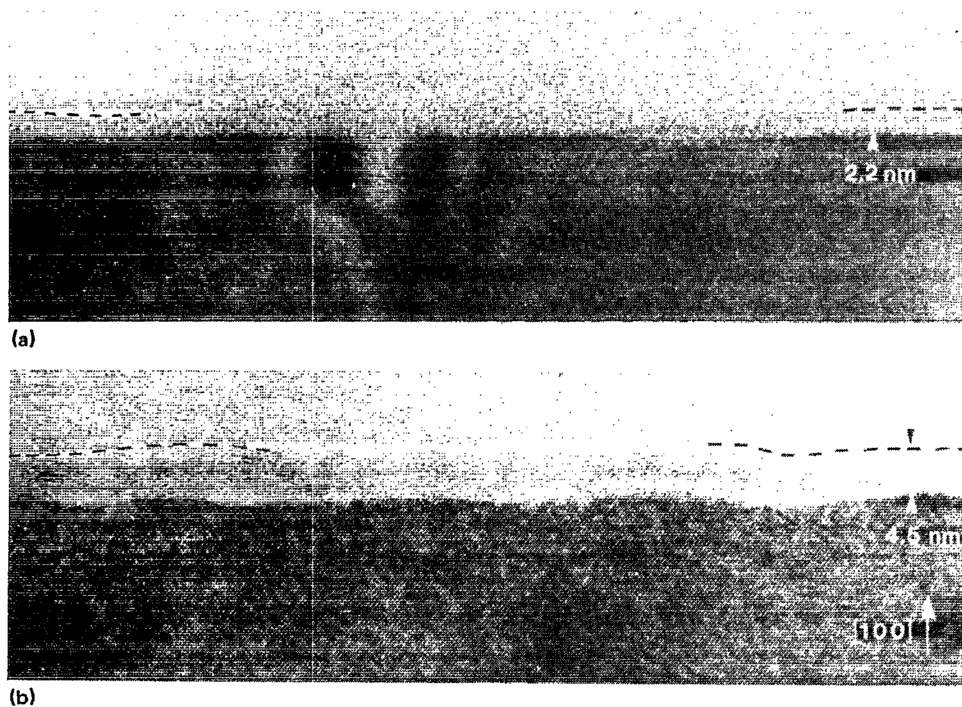

FIG. 3. High-resolution TEM micrographs of the surface of samples after etching at (a) 0.5 W/cm^2 and (b) 1.0 W/cm^2. The arrows indicate the amorphous layer thickness.

extremely sensitive to damage. PLI of undoped InP samples is reduced to about 0.3 of the original signal, normalized as 1.0, after RIE at 0.5 W/cm^2. After removal of 10 nm by anodic oxidation PLI is restored to 1.0.

To investigate deep penetration of damage we have RIE etched a layer of InP on top of a 0.1-μm-thick InGaAsP layer such as that used for laser fabrication. The RIE power was 0.5 W/cm^2 and the PLI was measured as a function of the remaining InP layer thickness. The PLI of this layer decreases only when the remaining InP on top is less than 20 nm thick (the resolution of the layer thickness measurement), so there is no visible damage penetrating deeper than this. The PLI data confirm that little damage is caused by the etch process and this damage is probably confined to the top 10 nm or less. Also double-channel-planar-buried-heterostructure lasers made by RIE perform equally well as lasers made by wet chemical etching without additional cleaning steps.

The increase of the amorphous layer thickness with power suggests a mechanism in which InP is transformed from crystalline to amorphous structure by physical impact. Comparing with a thermodynamical calculation,[17] it is found that if chlorine is deficient at the surface, formation of $InCl_2$ or $InCl_3$ takes place. At 200 °C the $InCl_x$ evaporates quickly leaving a surface enriched in P, although P, in the form of P_4, has a higher evaporation rate than $InCl_x$. Possibly the formation of volatile P compounds is slower than that of $InCl_x$. Clearly the removal of P is not ion enhanced, because the P-enriched layer increases and the etch rate remains equal at higher power.

In conclusion, a chlorine-based dry-etch process for InP has been developed that shows a high anisotropy and a fairly high etch rate. Straightforward thermodynamic calculation gives insight in the etching mechanism. Contrary to what is generally expected this RIE process induces very limited damage in the material and no evidence of damage at depths exceeding 10 nm is found. On the basis of these results we conclude that RIE of InP using a chlorine-based etch as described here is very suitable for optoelectronic applications.

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