Influence on semiconductor junctions.—In order to investigate the possibility of deleterious effects caused by I_2-solvent quenches on devices, leakage currents of silicon detector diodes were measured following such treatment. These n-p diodes are large area, 10,000 ohm-cm resistivity mesa devices and as such are very sensitive to surface effects. Leakage currents of these diodes given either an I_2-methanol or an I_2-carbon tetrachloride quench following a 5-sec HNO_3-HF (40-1) etch displayed no degradation. Results after 10-min cycling in dry O_2 and wet N_2 did not differ from those obtained on control diodes. This would indicate that the iodine surface treatment did not degrade the electrical characteristics of these sensitive junctions.

Conclusions

The technique of I_2-nonaqueous solvent quenching has been investigated, and preliminary experiments indicate that it will temporarily prevent oxide, hydroxide, and fluoride formation normally experienced in silicon technology. This has been demonstrated by low-energy electron diffraction studies and by the application of the technique to several device processing procedures. Since the iodine films are readily removed, the procedure serves as a simple means of preparing atomically clean surfaces just prior to device processing.

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Enhanced GaAs Etch Rates Near the Edges of a Protective Mask

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It has been observed in the author's laboratory that holes etched into gallium arsenide through windows in a protective silica etch mask are deeper near the edges of the mask than at the center of the hole. This phenomenon is illustrated by the angle-lapped section shown in Fig. 1. It is obvious from the morphology of the hole bottoms that the etch rate was greater near the mask edges than at the centers of the holes. This "edge effect" presents a severe problem to the fabrication of device structures by selective etch and deposition techniques.

The edge effect occurs when GaAs holes are etched with such etchants as bromine-methanol (1:1000), hydrogen peroxide-sulfuric acid-water (1:5:1), and 3% sodium hypochlorite solutions. It is also observed to a lesser degree with holes formed by HCl vapor etching at temperatures up to 800°C. The magnitude of the effect tends to decrease as the hole depths increase, *i.e.*, the deeper holes have flatter bottoms. The phenomenon is independent of the window dimensions with the exception that with very small windows the regions of enhanced etch rate near opposite walls may overlap.

The enhanced etch rates near the mask edges could be due either to localized stresses occurring at the mask-GaAs interface or to surface diffusion of adsorbed molecules along the protective mask which effectively results in a greater flux of etchant at the mask edges. As will be shown below, the experimental results provide strong support for the surface diffusion explanation.

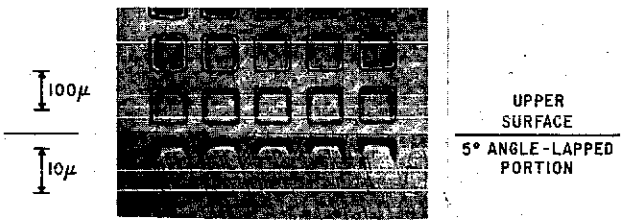

Fig. 1. Micrograph showing 5° angle-lapped section through holes etched into GaAs with an unstirred bromine-methanol (1:1000) solution.

Stresses present at the mask-GaAs interface could be related to the differences in thermal coefficients of expansion between the silica film and GaAs. They would be imposed when the silica-coated GaAs crystal is cooled from the 450°C silica deposition temperature (oxidative tetraethyl orthosilicate process) to room temperature. To investigate further the effect of stress at the mask-GaAs interface, a polymerized KMER (Kodak Metal-Etch Resist) etch mask was employed. This mask was applied to the GaAs crystal at room temperature, but in this case also the edge effect was still present at the etched holes. Later a silica etch mask obtained by a room temperature, tetraethyl orthosilicate, glow discharge process was employed. Since the holes were then etched at room temperature, the effects of stress at the mask-GaAs interface should be minimized. However the etch rates were still greater near the mask edges than toward the center of the hole.

When a masked GaAs slice is placed in contact with the etchant, the etchant molecules are striking the protective mask as well as the GaAs exposed at the windows. Some of the molecules which strike the protective film are adsorbed and migrate across the surface for some distance before desorbing. A portion of these molecules will diffuse to the exposed GaAs and may react causing dissolution. Thus the exposed GaAs near the mask edge is receiving etchant molecules from surface diffusion as well as by "direct" diffusion. If the etch rate were limited by diffusion of etchant molecules to the reaction surface, then the above-mentioned process would result in an enhanced initial etch rate near the mask edge as compared with the etch rate near the center of the hole. This explanation is supported by the shapes of the hole bottoms shown in the angle-lapped section of Fig. 1. The holes on either side of the array have unsymmetrical edge effects, *i.e.*, the etch depth is greater near the edge having the largest adjacent area of protective mask. Since these edges have greater adjacent mask areas, they receive more etchant molecules from sur-

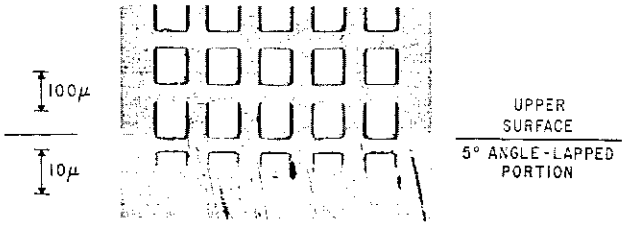

Fig. 2. Micrograph showing 5° angle-lapped section through holes etched into GaAs with a 0.7M H_2O_2-1M NaOH solution.

face diffusion. The three inner holes exhibit equal and symmetrical edge effects because they have equal adjacent mask areas. The exposed regions near the corners of the windows have the greatest adjacent mask areas and would be expected to exhibit the greatest edge effect. This is confirmed experimentally by observation of the hole bottom contours with an interferometer. It should be noted that the greatest contribution of etchant molecules due to surface diffusion would be realized at the initial stages of etching. This is in agreement with the experimental observation that the magnitude of the edge effect decreases with increasing hole depth.

It has been found that the etch rate of GaAs with a 0.7M hydrogen peroxide-1M sodium hydroxide solution is limited by the rate of chemical reaction rather than by the diffusion rate (1). If surface diffusion of adsorbed molecules along the protective mask is responsible for the enhanced GaAs etch rates near the mask edge, then the effect should be eliminated by etching with the above mentioned H_2O_2-NaOH solution. Figure 2 shows an angle-lapped section through GaAs holes formed by etching with this solution. The holes have flat bottoms, and no evidence of an enhanced etch rate near the mask edge is noted. These results provide strong support for the explanation of the edge effect based on surface diffusion of etchant molecules adsorbed on the protective mask.

Acknowledgments

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Brief Communications

The Effect of Concentration on the Interdiffusion Coefficient of Chromium in Chromium-Iron Alloys

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An investigation into the mechanism of oxide formation of chromium-iron alloys for a temperature range 800°-1200°C has resulted in determinations of the interdiffusion coefficients of chromium. The concentration profiles of chromium in the alloy were measured using an electron probe microanalyzer and metallographic techniques. The results which are presented in Fig. 1 exhibit a minimum value of diffusivity at 60% chromium concentration for a temperature of 1000°C. The values of Gorbunov *et al.* (1) for chromium concentrations of 84.5% and 29.4% Cr at 1000°C agree well with these data. Krwoglaz and Smernov (2) have indicated that the phenomenon of exhibiting minimum values is not common, but has been observed for diffusion in β-brass. Some anomalous predictions of chromium-iron behavior in their alloys may be attributed to the use of average values of interdiffusional coefficients over the range where a minimum exists. Here it is particularly important to use the discrete values reported.

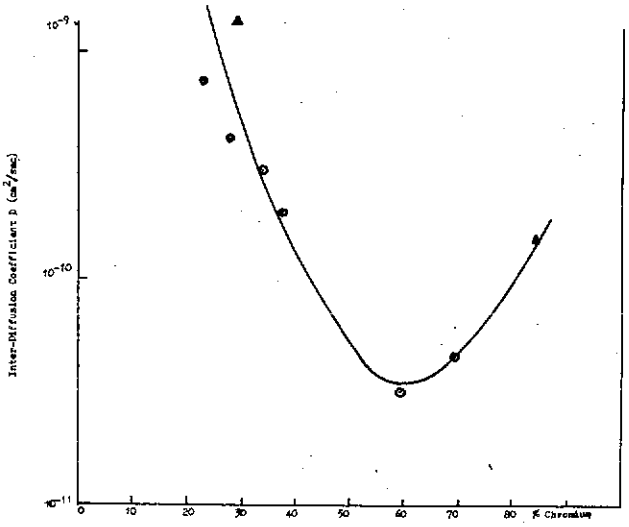

Fig. 1. Plot of diffusion coefficient vs. chromium concentration. △, Gorbunov; ⊙, authors.

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