Chemical Cleaning of GaSb (1,0,0) Surfaces

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ABSTRACT

GaSb (1,0,0) surfaces have been cleaned by chemical passivation and later heat-treatment in ultrahigh vacuum conditions. Four different etching solutions consisting of an oxidant and an acid for oxide dissolution have been studied. With the H_2SO_4:H_2O_2:H_2O the surfaces become very rough, unevenly covered with oxides, and not suitable for later epitaxial growth. The remaining three etchants studied, HCl:H_2O_2:NaK(tartrate), HF:HNO_3:CH_3COOH, and Br:methanol, leave rather smooth surfaces covered with a thin passivating layer, probably consisting of pure Sb, Sb_2O_3, and Ga_2O_3, which can be easily removed by heating the samples in ultrahigh vacuum at temperatures between 480° and 510°C.

One of the crucial stages in epitaxial growth or in the preparation of negative electron affinity (NEA) photocathodes is the preparation of clean and flat surfaces. In both cases the presence of contaminants, mainly carbon, must be carefully prevented. In the case of NEA photocathodes the presence of small amounts of C on the surface rapidly degrades the efficiency. In molecular beam epitaxial growth if some residual C remains on the surface, this cannot be removed unless the samples are heated at rather high temperatures. For GaAs, temperatures well over the limit of congruent evaporation are necessary and this treatment causes the faceting of the surface.

In the past, argon ion bombardment and later annealing were used for cleaning the semiconductor surfaces. However, the temperature needed for damage recovery is well over the congruent evaporation temperature again and this process is not suitable for surface preparation. At present, an alternative process consisting of passivating the GaAs surface with a thin oxide layer which prevents C adsorption is commonly used [see for example Ref. (1)]. This thin layer can be easily removed by later heating the sample in ultrahigh vacuum conditions. The etching of the sample takes place via the typical oxidation-dissolution chemical mechanism. The formed oxide is dissolved in some aqueous acid or basic solution. After stopping the chemical reaction the sample surface remains covered with a thin oxide layer, that because of its chemical inactivity prevents the adsorption or reaction of possible contaminants like C on the surface.

Unfortunately GaSb is more reactive than GaAs and thus GaSb is quickly oxidized in an oxidant ambient. Moreover, the Sb oxides are rather insoluble in aqueous acid or alkali solutions causing inhomogeneities during etching when the oxidation-dissolution mechanism is responsible for the etch reaction. The presence of some complexing agent that renders the oxidized Sb soluble during the etching has been proposed (2).

In this work we report results obtained with several etching solutions. Morphology, Auger measurements, and RHEED have been used to demonstrate the suitability of some of these etchants.

Experimental

The samples used in this work are (1,0,0) polished GaSb slices doped with Te (3×10^{17} cm^{-3}) obtained from ingots grown on silica boats by the horizontal gradient freeze technique.

Except for the last etch step all the samples have been subjected to the same cleaning procedure. First of all they are degreased in boiling trichloroethylene, acetone, methanol, and rinsed in deionized water. The residual oxides on the sample surfaces are etched off by HCl and later rinsed in deionized water to achieve the same starting conditions in all of the samples. After that, the samples are immersed in H_2SO_4 to remove possible organic residues, and then rinsed again in deionized water. Finally, the samples are etched in the different freshly prepared solutions. The final etch is quenched by successive immersion of the samples in two different methanol baths. After completing the cleaning procedure, the samples are blown with filtered dry nitrogen, soldered with Ga to a molybdenum sample holder, and loaded into a 360 MBE Varian system. During all the cleaning sequences, the samples never become exposed to air until they are dried with N_2.

The compositions, temperatures and etch times of the different etchants are the following:

1. H_2SO_4:H_2O_2:H_2O, (3:1:1), 70°C, 2 min
2. HCl:H_2O_2:NaK(tartrate), (830 m*M*:300 m*M*:83 m*M*), room temperature, 5 min
3. HF:HNO_3:CH_3-COOH, (1:10:15), room temperature, 15s
4. Br:methanol, (5:1000), room temperature, 30s

Once the samples are loaded in the vacuum system and the limiting vacuum achieved, they are heated to obtain a clean surface. Over 400°C, the samples are heated under a Sb flux in order to avoid surface decomposition. Auger spectra and RHEED diffraction patterns were recorded at 50°C steps. This study has been repeated for two samples prepared with each of the etching solutions mentioned above except in the case of the H_2SO_4:H_2O_2:H_2O mixture.

Another series of samples were prepared in the same way for studying the surface morphology by scanning electron microscopy in the amplitude modulation working mode for enhancing the contrast.

Results and Discussion

Morphology.—Figure 1a shows the electron microscope photography of a sample etched with H_2SO_4:H_2O_2:H_2O. As is clearly apparent, the surface is considerably roughened as a consequence of a very inhomogeneous etch. Moreover, even at first sight, differently colored regions can be seen unevenly shared over the etched surfaces. These effects may be due to the formation of a passivating oxide which is rather insoluble in acid or alkali aqueous solutions (2) which prevents the later etch of the sample as it has been proposed by Buglass *et al.* (3). The oxide island formation has also been observed in the first stages of the anodic oxidation process in GaAs, InP, InAs, and InSb (4).

In Fig. 1b the micrograph of a sample etched with HF:HNO_3:CH_3COOH can be seen. Contrary to that in the above case, the surfaces observed by the electron microscope are rather smooth and show a mirror-like aspect at

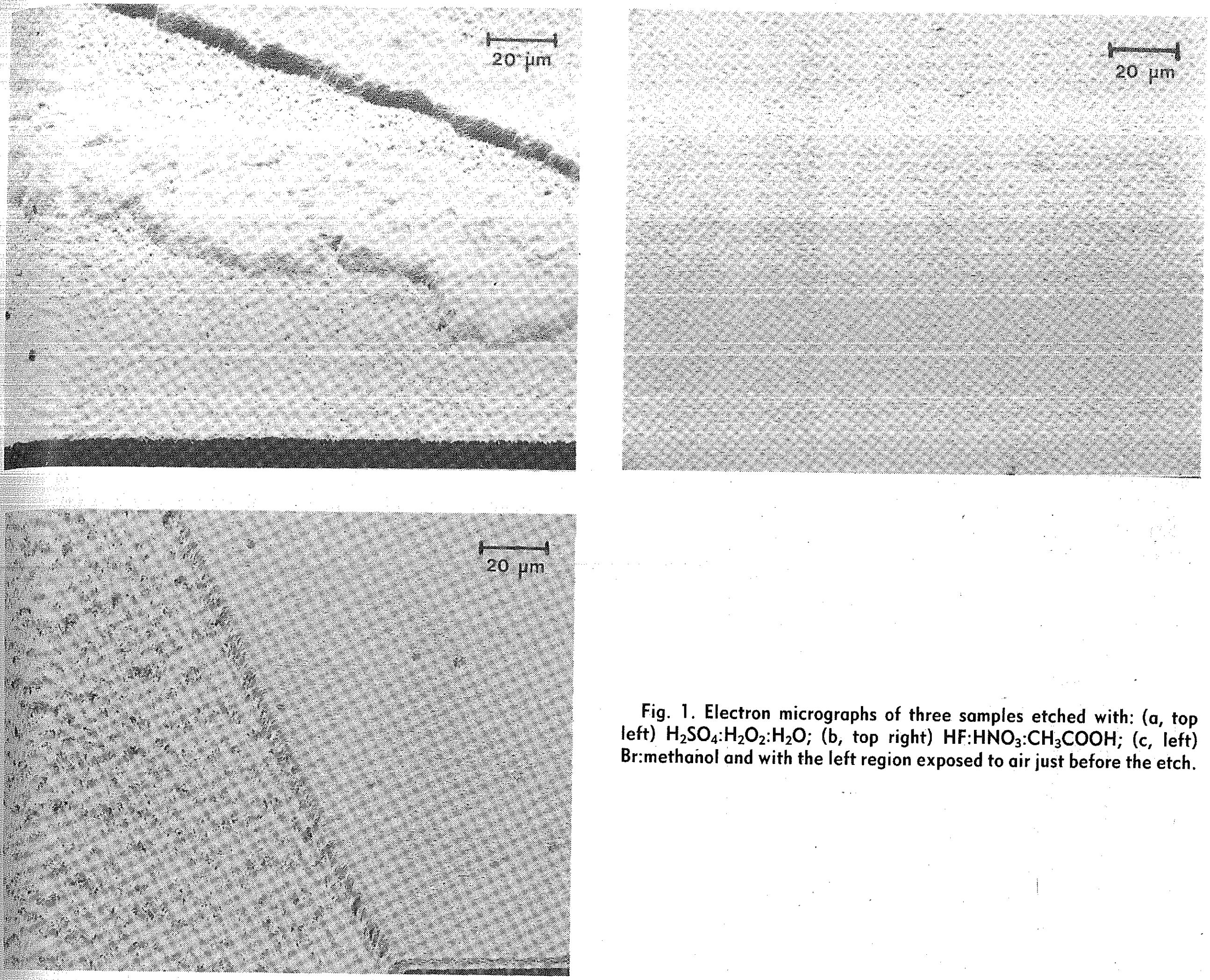

Fig. 1. Electron micrographs of three samples etched with: (a, top left) H_2SO_4:H_2O_2:H_2O; (b, top right) HF:HNO_3:CH_3COOH; (c, left) Br:methanol and with the left region exposed to air just before the etch.

first sight. The results with the remaining two etching solutions, HCl:H_2O_2:NaK(tartrate) and Br:methanol are very similar to that obtained with the HF:HNO_3:CH_3COOH etchant, and even the degree of roughness observed with the electron microscope is comparable, and thus they will not be shown here.

Special care has to be paid so as to avoid exposing the samples to air during all the cleaning process, otherwise the exposed area becomes severely damaged. In Fig. 1c the electron micrograph of a sample, etched with Br:methanol, with exposed and unexposed areas can be seen. The left side of the micrograph corresponds to a region which has accidentally been put in contact with air just before the etch. As seen, a step between exposed and unexposed areas has developed. Furthermore, the exposed region results in a very much rougher surface than the unexposed one and, even by simple visual inspection, it can be seen that the exposed area has lost its mirror-like aspect. To the contrary, the region at the right side of Fig. 1c exhibits a rather smooth aspect comparable to that of Fig. 1b indicating that this region has suffered an etch more homogeneous than the exposed area. Probably, during the exposure to air a strong electrochemical potential is developed between the exposed and unexposed areas which causes a quick and inhomogeneous oxidation of the region in contact with the ambient. Thus, because of the poor solubility of the oxide, the sample becomes unevenly and selectively etched giving rise to a very rough surface. Similar effects are observed when the samples to be etched with the HCl:H_2O_2:NaK(tartrate) solution are previously put into contact with air.

In view of the morphology results obtained with the H_2SO_4:H_2O_2:H_2O solution described above, only the samples etched with the three remaining mixtures have been studied by RHEED and Auger.

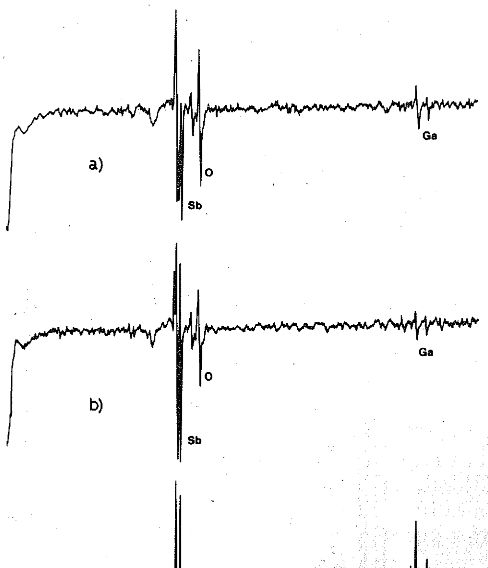

Fig. 2. Auger spectra of a sample etched with Br:methanol: (a) as introduced in the vacuum system; (b) after 5 min electron bombardment in the same point and with no thermal treatment; (c) after completing the thermal treatment.

Auger measurements.—Figure 2a shows a typical Auger spectrum of a sample etched with Br:methanol before any thermal treatment. The only peaks observed correspond to Sb, O, and Ga. In some cases traces of C appear. The spectra obtained in the samples etched with the other solutions before thermal treatment are similar. First of all, it should be remarked that the Sb peak observed in the as-prepared samples does not have the standard shape of pure Sb (5) nor that obtained in clean GaSb (see Fig. 2c). When the samples are heated, the Sb lineshape changes in such a way that it can always be represented as the superposition of two bands of similar shape but different amplitudes: one at an energy about 454 eV, as normally observed in pure Sb or clean GaSb, and another analogous band shifted about 5-6 eV towards lower energies and probably due to some oxidized species of the Sb. The superposition of both bands results in the shape observed in all the etched surfaces (see Fig. 3). This apparent superposition of two peaks has also been observed in oxidized samples of InSb (6). The energy separation between the two bands is such that the height of the rightmost peak of the complex band, h2, corresponds to pure Sb and is not affected by the proximity of the shifted band. In a similar way, the leftmost peak height, h1, of the complex band is not affected by the presence of the standard lineshape and it can be taken as a measure of the shifted band.

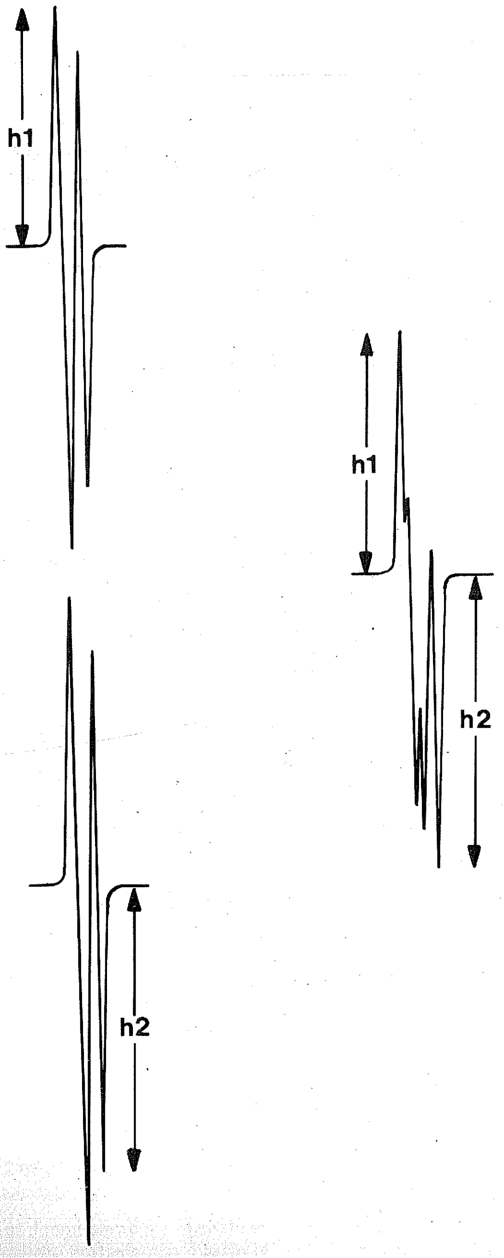

Fig. 3. Superposition of shifted Auger peaks giving rise to the lineshapes observed for Sb. See text.

Table I. Auger peak heights for the different as etched samples

Sample	Etchant	h1 Sb	h2 Sb	h_{p-p} O	h_{p-p} Ga
30	Tartrate	14.4	17.6	52.8	15.2
31	Tartrate	8.5	10.5	57.5	23.5
32	HF	11.2	19.4	49.5	19.9
34	HF	14.4	25.1	42.2	18.2
33	Br	19.2	35.7	32.4	12.6
35	Br	26.2	25.5	36.2	12.1

The differences among the Auger spectra recorded in the different as-prepared samples are summarized in Table I. The peak heights h1 and h2 corresponding to Sb and the peak-to-peak amplitudes of O and Ga are reported. Each height has been normalized to the sum of the four peaks. The most significant difference is concerned with the Sb content (pure as well as oxidized) of the distinct samples. This content is maximal in the samples etched with Br:methanol and minimal in those prepared with $HCl:H_2O_2:NaK$ (tartrate).

The cleaning process during heating has been followed by recording, at each temperature, the peak-to-peak amplitude, h_{p-p}, for Ga and O and the heights h1 and h2 for the two Sb species. These heights have been corrected by the sensitivity factors of the different elements [see Ref. (5)]. In the case of Sb, an additional correction, which takes into account the ratios of h1 and h2 with respect to h_{p-p}, has been introduced. Finally, each height has been normalized to the sum of the four. This normalization process enables us to obtain better insight into the composition of the surface layer, although these results only can be considered in a qualitative way. Figure 4 shows the evolution of the different peaks with temperature for samples prepared with Br:methanol and $HF:HNO_3:CH_3COOH$.

Although the behavior of all the samples is very similar, in the sample represented in Fig. 4a the evolution of the different peaks with temperature can be more easily followed than in the other samples because of the higher initial Sb content and because the Auger spectra have been recorded at the smallest temperature intervals. We can distinguish six temperature regions that are clearly differentiated:

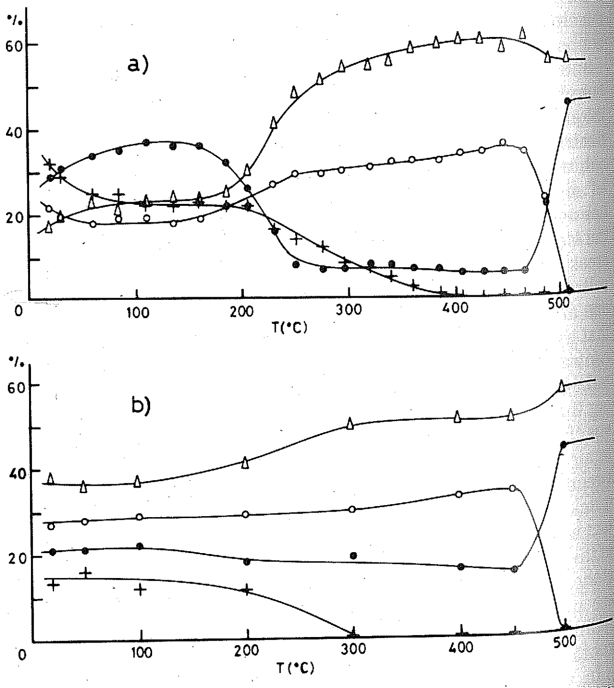

Fig. 4. Surface layer composition evolution *vs.* temperature for two samples etched with: (a) Br:methanol; (b) $HF:HNO_3:CH_3COOH$ (○: O; ●: pure Sb; +: oxidized Sb; △: Ga).

1. Between room temperature and 80°C, the Sb oxide peak decreases while the pure Sb peak grows, indicating that a certain amount of the oxide is reduced. However, this oxide reduction may be due not only to a temperature effect, but more probably to an oxide reduction induced by the electron bombardment during the initial stages of the Auger spectra recording. In other samples we have observed a similar decrease of the Sb oxide peak at room temperature. The spectrum of Fig. 2b has been recorded under the same conditions as that of Fig. 2a after maintaining the electron beam focused at the same point for about 5 min.

2. Between 80° and 160°C no appreciable change seems to occur.

3. As the temperature increases above 160°C, the peak due to pure Sb starts to decrease reaching a minimum value, clearly distinguished from the noise level, at around 250°C. This pure Sb decrease is accompanied by a quick growing of the Ga peak.

4. Between 200° and 400°C a gradual and complete elimination of the Sb oxide takes place. In this temperature range the Ga peak continues to grow, although more slowly than in the above region. Since the oxide elimination takes place over a wide temperature range, an explanation via a desorption process does not seem suitable. A mechanism completely analogous to that which occurs during thermal annealing of the anodic oxide of GaSb as proposed by Schwartz *et al.* (7) may be argued. Near the GaSb interface a Sb_2O_3 reduction giving rise to Ga_2O_3 and metallic Sb could take place via the reaction Sb_2O_3 + 2GaSb Ga_2O_3 + 4Sb. Later, the pure Sb out diffuses reaching the surface. The pure Sb evaporates from the surface in such a way that once a certain rate is achieved, the surface becomes depleted of pure Sb and the overall process can continue.

5. Above 400°C and up to around 460°C the surface layer consists almost exclusively of Ga oxide. The small Sb signal observed may be due to a small amount of pure Sb dissolved in the Ga oxide. However, it seems more probable that this signal comes from the GaSb substrate, because at these temperatures the vapor pressure of Sb is high enough to completely deplete pure Sb from the surface layer.

6. Between 480° and 510°C the Ga oxide desorbs quickly leaving a clean GaSb surface. Figure 2c shows an Auger spectrum of a sample surface cleaned in such a way.

In some of the as prepared samples traces of C appear. However, in all of the cases these traces disappear completely above 250°C. In all of the samples a small peak due to S has been seen at the final stage of the cleaning process. This small S signal is seen just when the O peak starts to decrease, however it disappears immediately. It is possible that some S residual contamination coming from the H_2SO_4 bath before the final etch could have remained at the surface.

As has been pointed out above, the pure Sb peak height never becomes null but remains small probably due to the contribution of electrons escaping from the GaSb substrate across the surface layer. This height, just before the elimination of the Ga oxide, can enable us to estimate and compare the oxide thickness obtained with the different etchants. This thickness is maximum in the samples etched with Br:methanol and minimal when the etching solution is $HF:HNO_3:CH_3COOH$. Furthermore, it is apparent a certain correlation exists between the oxide thicknesses estimated in this way and the temperature which is needed for completely removing the oxide layer. Whereas in the samples etched with Br:methanol, and thus with the thickest oxide, a temperature between 500°-510°C is necessary for oxide elimination, in the samples prepared with $HF:HNO_3:CH_3COOH$ a completely clean surface is obtained at temperatures between 480° and 490°C, slightly lower than the above ones.

Thus, although from this study we cannot infer conclusively which are the species formed during the chemical etch, it seems reasonable to assume that the surface layer consists of Ga_2O_3, Sb_2O_3, and Sb as it has been observed in GaSb oxidized by other methods. These are the only chemical species formed in thermal or anodic oxidation processes unless the conditions are highly oxidizing (4, 7). Furthermore, the behavior of the thermal or anodic oxides under thermal annealing is very similar to the one reported here.

Fig. 5. RHEED diffraction pattern after completing the thermal treatment.

RHEED.—No diffraction pattern is observed in the as-prepared samples. After reaching 400°C and under Sb flux spotty patterns start to be observed although only in those samples which show the largest Sb peak heights at that temperature. This seems to corroborate that in these samples the oxide thicknesses are the lowest.

After completely removing the oxide layer a bar diagram with 1/3 order streaks along the $[1,\bar{1},0]$ azimuth (Fig. 5) can be observed in all the samples indicating that the surface is atomically flat (8).

Conclusions

Among the four chemical etchants ($H_2SO_4:H_2O_2:H_2O$; $HF:HNO_3:CH_3COOH$; $HCl:H_2O_2$:NaK(tartrate); Br:methanol) used for obtaining clean and flat GaSb surfaces under ultrahigh vacuum conditions, the first one must be discarded because it gives rise to very rough surfaces. This may be the most oxidizing of the four and, because of the poor solubility of the oxides, the surface is unevenly etched and remains inhomogeneously covered with oxides after the etch. The remaining three solutions produce rather flat surfaces when the samples never come into contact with air between the preliminary degrease and the final etch. These three etchants give rise to a thin surface layer which probably consists of Ga_2O_3, Sb_2O_3, and pure Sb, and whose proportion depends on the particular etchant used. This thin layer prevents C adsorption on the sample surface during preparation and loading into the UHV chamber.

This surface layer can be easily removed by heating the samples at temperatures between 480° and 510°C, leaving atomically flat surfaces when the samples are maintained under a Sb flux during the final stage of the heat cleaning process. The elimination of the surface oxide takes place in two stages. First, the Sb_2O_3 at the interface is reduced increasing the Ga_2O_3 content and leaving pure Sb which outdiffuses towards the surface from where it is evaporated. Later the Ga_2O_3 layer is quickly desorbed leaving a clean and flat GaSb surface.

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Electrical and Metallurgical Characterization of Niobium as a Diffusion Barrier Between Aluminum and Silicon for Integrated Circuit Devices

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ABSTRACT

Electrical, metallurgical, electromigration, and functional characterizations of an (Al-0.5% Cu)/Nb interconnect metallization for use in 1.2 μm SRAM integrated circuit devices have been performed. The results indicate that niobium is an excellent diffusion barrier to aluminum and silicon. It is shown that the presence of niobium has significantly improved the electromigration strength (at j = 1.0E7 A/cm^2) and the thermal and electrical stability of metal to silicon and metal to metal contacts. The barrier characteristics of the niobium were studied electrically (via junction leakage current and contact resistance measurements) and analytically (via TEM examination of aluminum-niobium-silicon interfaces). TEM and electron diffraction analyses show the formation of the $NbAl_3$ phase. It is found that the $NbAl_3$ phase has a much slower rate of growth than $TiAl_3$ in the temperature range studied. Results do not indicate any significant increase in junction leakage current of contact resistance after 540 min of heat-treatment at 425°C. The results further indicate that the niobium does not have any negative effects on the performance of 1.2 μm CMOS SRAM devices. It appears, however, that the presence of niobium has an effect on the speed distribution of the devices.

Aluminum and its alloys containing silicon and copper are widely used for the interconnecting metallization of integrated circuit devices. Silicon is added to the saturation point of the aluminum film at the alloying temperature, hence eliminating aluminum spiking into the silicon substrate at the contact areas. The addition of copper is primarily to improve the electromigration strength of the aluminum film and suppress the formation of hillocks. The addition of these two alloying elements, however, can cause some severe reliability and processibility problems (1-7).

The ever increasing demand for high performance integrated circuit devices has resulted in a significant scaling of device geometries. This scaling consists of reduction in diffusion junction depth, contact size, and dimensions of the interconnecting metallization film. The more shallow the junction, the higher the possibility of junction leakage or shorting if an aluminum-silicon alloy is in direct contact with a silicon substrate. Another consequence of direct contact between the silicon substrate and aluminum-silicon interconnecting films is the regrowth of epitaxial silicon at contacts resulting in an increase in contact resistance and degradation of circuit performance (8-10). Therefore, one cannot obtain metallurgically and electrically reliable metal to silicon contacts using only silicon containing aluminum films in direct contact with a single-crystal silicon substrate. Consequently, it is essential to use a silicon-free aluminum alloy in conjunction with a suitable diffusion barrier as an interconnecting metallization film.

Various refractory metals and their alloys have been evaluated as diffusion barriers between aluminum and silicon. There is a great deal of information in the literature regarding the kinetics and thermodynamics of their reactions with aluminum and its alloys (11-14). The authors also have studied the metallurgical and electrical characteristics as well as the reliability of an (Al-0.5% Cu)/Ti interconnect metallization system for use in 1.2 μm CMOS SRAM integrated circuit devices (15).

Although there is a great deal of information regarding various refractory diffusion barrier elements and their applications and limitations in the literature, studies are continuing to investigate more metallurgically and electrically reliable barriers with less process complications and fewer limitations. Among the refractory metals studied as diffusion barriers for the fabrication of integrated circuit devices, niobium (Nb) is the least explored, if it has been explored at all. Niobium has a very high melting temperature (2468°C) which makes it thermally a very stable diffusion barrier. Because of such a high melting point, it does not exhibit self-diffusion at temperatures below its recrystallization temperature (1/2 Tm); consequently, it is not susceptible to electromigration at post-metal processing temperatures. Moreover, the resistivity of niobium is only approximately six times that of aluminum (16) which makes it a possible candidate for the main conductor in a multilayer metallization system.

This paper presents the results of a study conducted on an aluminum (containing 0.5% Cu)-niobium (Nb) bilayer interconnecting metallization structure used for the fabrication of 1.2 μm minimum geometry CMOS SRAM integrated circuit devices. In this study, metallurgical and electrical properties of this bilayer film are evaluated along with its electromigration strength.

Experimental

The evaluation and characterization of niobium as a diffusion barrier in an (Al-0.5% Cu)/Nb system consisted of four parts. In part A, the extent of metallurgical interaction at the interfaces between the niobium and Al-0.5% Cu films, and the niobium and silicon dioxide films or single-crystal silicon substrate after heat-treatment for 30, 120, and 240 min at 425°C in a hydrogen environment was studied. To examine interactions at various film interfaces, a Philips EM420T transmission electron microscope equipped with a Tracor TN-5500 EDS System was used. This microscope has resolutions of 2, 15, and 25Å in the TEM, STEM, and SEM modes, respectively. To identify the phases present at various interfaces, a convergent beam electron diffraction technique was used. With such a

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