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Short Note

New fast chemically assisted ion beam etching (CAIBE) technique for preparation of TEM specimen from silicon

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Résumé. — Nous avons utilisé l'amincissement ionique assisté chimiquement pour préparer des échantillons de silicium (111), ausssi bien en coupes planes que transversales, à l'observation en microscopie électronique à haute résolution. Pour cela, un flux d'iode gazeux est dirigé sur l'échantillon à amincir en même temps qu'un faisceau d'ions Ar^+ attaque la surface sous incidence rasante ($<20°$). L'amincissement résulte alors de l'érosion ionique et de la réaction chimique entre l'iode et le silicium. Cette technique permet d'accroitre considérablement la vitesse d'amincissement : la présence du flux d'iode gazeux permet de multiplier par 4 la vitesse d'érosion obtenue uniquement par le faisceau d'ions Ar^+. D'autre part, la frange transparente observable en microscopie électronique à transmission augmente fortement lorsque l'iode est utilisée : une aire transparente de près de $1mm^2$ a pu être obtenue alors qu'elle ne dépasse pas quelques μm^2 dans les conditions standard d'amincissement. L'observation en microscopie électronique à haute résolution des échantillons a permis de vérifier qu'aucun artéfact n'est introduit lors de la préparation. L'analyse Auger a permis de montrer l'absence de contamination par l'iode de la surface des échantillons amincis.

Abstract. — A new fast Chemically Assisted Ion Beam Etching (CAIBE) technique is reported for the preparation of silicon plane view and cross-sectional samples for high resolution transmission electron microscopy (HREM) without any detectable artefacts. In this technique a flux of iodine vapours derived from an ampoule of elemental iodine is directed on the sample surface (mechanically thinned to <50 μm) along with Ar^+ ion beam at a shallow angle. The etching (thinning) is obtained by combination of physical sputtering and chemical process, thus higher etch rate anf large electron transparent area are obtained. In the presence of iodine the etch rate is increased by a factor of 3-4 times in comparison to only Ar^+ ion beam under identical conditions. No artefacts are introduced due to the presence of iodine as confirmed by HREM and surface analysis studies.

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1. Introduction.

During the last few years great progresses have been made in improving the capability of transmission electron microscopy (TEM) in terms of its analytical power and ease of operation. The artefact free specimen preparation for TEM studies is always being a tedious, lenghtly and difficult. In many cases, the use of this versatile technique is restricted due to the lack of proper specimen preparation technique to explore the fundamental and practical problems. The problem is more acute while working with crystalline materials e.g. semiconductors to study structures at atomic level. Considerable efforts have been made to optimize the techniques for TEM specimen preparation [1-5] and at present majority of TEM specimens in materials science are prepared by reducing the initial thickness to 30-50 μm by mechanical polishing and final thinning is done by inert ion beam etching (IBE) at a shallow angle of beam incidence. Though it is possible to obtain satisfactory specimens by inert ion beam etching, some inherent problems exist e.g. low thinning rate, poor selectivity, redeposition, differential etching rates etc. [4-6]. Reactive gases are widely used in semiconductor industry [6-8] for ion beam etching to overcome these problems. But a little effort is made to use reactive gases for final thinning of TEM specimens. Recently Chew *et al.* [4] have used I^+ ion beam for preparation of TEM specimen from number of semiconductor materials and they obtained improved results in comparison to inert ion beam thinning.

The reactive gases can be used in different mode as illustrated in figure 1.

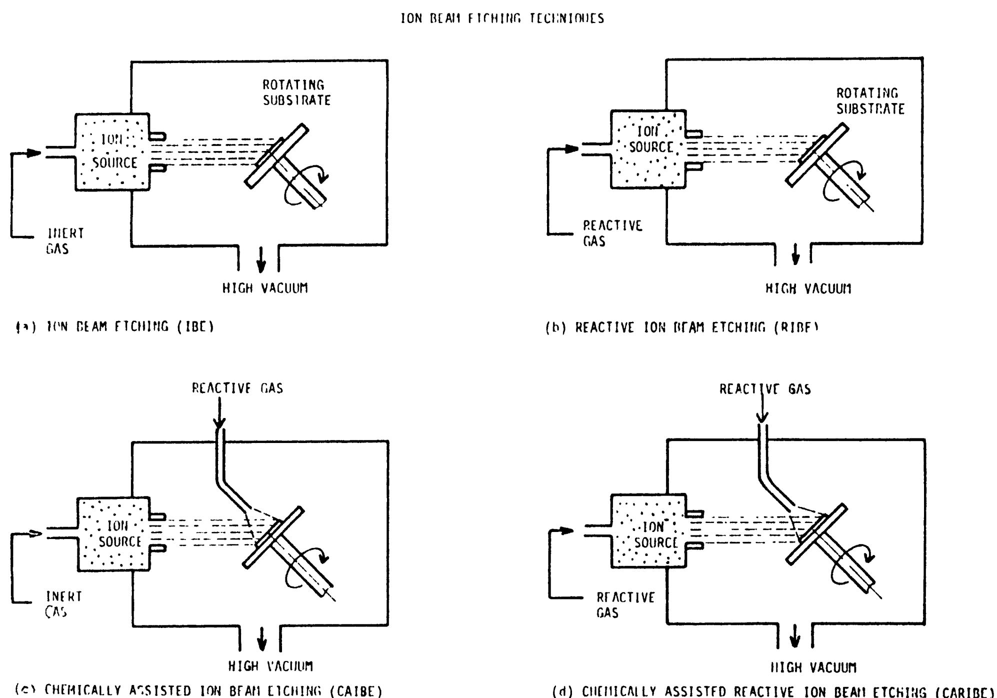

Fig. 1. — Ion Beam Etching Techniques.

First the Reactive Ion Beam Etching (RIBE) where the ion beam is produced by ionization of reactive gases, secondly Chemically Assisted Ion Beam Etching (CAIBE) where a flux of reactive

gas or combination of reactive gases is directed on the sample surface along with a ion beam of inert gas and third Chemically Assisted Reactive Ion Beam Etching (CARIBE) which is similar to CAIBE but ion beam of reactive gases is used. Higher etch rates are possible in these techniques as etching is produced by combination of physical sputtering and chemical reaction.

These techniques take advantage of chemical reaction without producing any surface contamination as volatile reaction products are formed which are removed by vacuum system. In RIBE the flux of reactive gas is limited by ion beam current density. CAIBE takes advantages of independent control of all etching parameters and no reactive gas is used in the ion source. Significantly low crystal damage has been reported [9] by CAIBE in comparison to IBE since part of ion beam energy is consumed in activating the surface chemical reaction between reactive gas and crystal surface to form volatile reaction products.

In this communication we report initial results on the preparation of TEM specimen from silicon monocrystal by CAIBE using reactive flux of iodine and Ar^+ ion beam. The Ar^+/I_2 CAIBE has been choosen for this study because iodine has advantage over other reactive gases (e.g. Cl_2, F_2, C_2F_6, CF_4, SF_6, O_2 etc.) used in ion beam etching: iodine is less reactive and toxic, it sublimes at room temperature, it is easy to produce and handle iodine vapours, iodine vapours can be trapped on simple cold trap without affecting the performance of the vacuum system. Thus it is possible to adopt Ar^+/I_2 CAIBE on standard commercial inert ion beam thinner without any major modification.

2. Experimental.

In this study boron doped Si(100) and Si(111) CZ monocrystals of resistivity 0.1- 1.25 ohms.cm were used. Prior to ion beam thinning, samples were mechanically polished to a thickness of 30-50 μm using different grades of abrasive papers. The schematic of experimental set up for Ar^+/I_2 CAIBE is shown in figure 2.

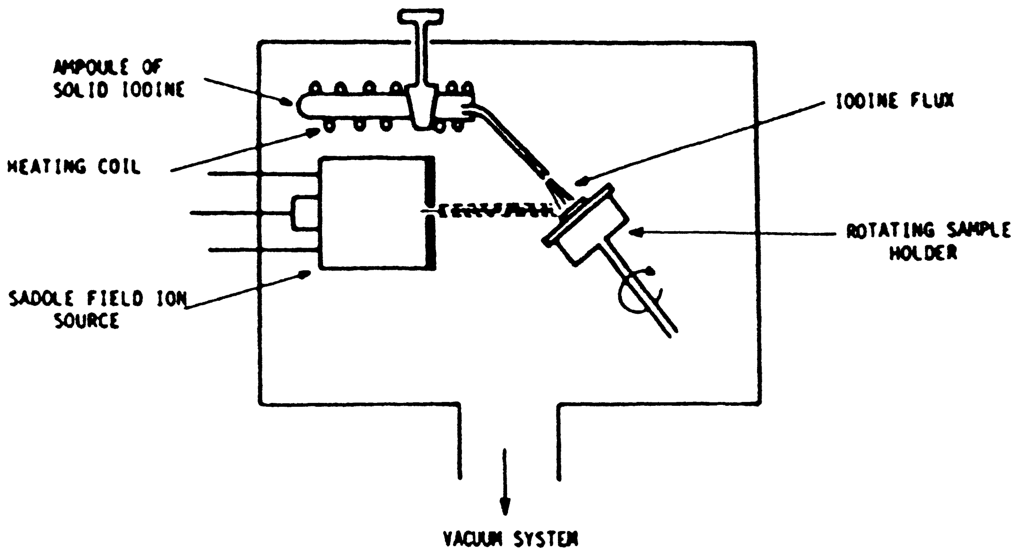

Fig. 2. — Schematic of Ar^+/I_2 Chemically Assisted Ion Beam Etching System.

The saddle field ion source is used and produces ion beam of about 3 mm^2 cross-section at the center of the specimen holder with Gaussian ion beam current density distribution. The reactive flux of iodine is derived from an ampoule of elemental iodine fitted with large aperture glass valve. The flow of iodine is controlled by resistance heating of iodine ampoule and adjusting the conductance of high vacuum valve.

The iodine ampoule is fixed inside the vacuum system to minimize the effect of environment temperature and condensation of iodine vapours in gas tube. A rotatable and tiltable sample holder is used. For mechanical stability, samples were mounted on a 3 mm nickel grid and tantalum plates of thickness 100 μm with 2 mm diameter aperture were used to hold and mask the sample. No sample cooling arrangment was available but it is observed that the temperature of the specimen remained below 50° C due to good thermal contact provided. The ion beam thinning was done by a 4 keV Ar^+ ion beam with an incidence of 17° and a current in the range 15-25 μA over cross sectionnal area of 3 mm^2. The samples were etched till the first appearence of the hole in the specimen. Final thinning was done by reducing the ion beam energy to 3 keV and the angle of ion beam incidence to 12°. Then, the back surface of the sample was etched a few minutes with only the inert ion beam to remove any physically adsorbed iodine. Etch rate measurements were made by depth profiling of etched area. The thinned specimens were observed under Philips CM-30 and JEOL 100 C electron microscopes.

3. Results and discussion.

To find the optimum flux of iodine for preparation of TEM specimen, the effect of iodine partial pressure on the etch rate of silicon has been studied at constant ion beam energy of 4 keV and at three different ion beam current densities. These current densities were calculated from sputterring rate measurements [10]. The results are shown in figure 3.

The etch rate of silicon strongly depends upon the iodine flux and increases steadly with iodine partial pressure in the range 2-8 $\times$ 10^{-5} Torr. When the iodine pressure is above 5 $\times$ 10^{-5} Torr, some surface roughness was observed this may be due to the high etching rate due to chemical process or non uniform flux of iodine vapours. Further increase of iodine pressure in the present study was limited by pumping speed of the vacuum system. The Auger Electron Spectroscopy and Energy Dispersive X-ray analysis of Ar^+/I_2 CAIBE etched silicon surface showed that there is no surface contamination due to the presence of iodine. The surface analysis of Ar^+/I_2 CAIBE etched silicon monocrystal was performed without any presurface treatment and backing of vacuum system to avoid possibility of removing any reaction products. But it is important to stop the iodine flux before the Ar^+ ion beam to avoid physical adsorbtion of iodine vapours on silicon surface, in the absence of ion beam. The etch rate measurements and surface analysis suggest that the reaction products of Si-Ar^+/I_2 CAIBE are highly volatile at room temperature. The removal of reaction products from the substrate surface is not rate limiting step but it is the availability of iodine flux on the silicon surface. Iodine has high atomic mass [1-3], so no experiments were performed to identify the mass spectra of reaction product as the upper limit of available gas analyser is 200amu. But the mechanism of Si-Ar^+/I_2 CAIBE can be explained on the basis of the mechanism proposed for si-Ar^+/Cl_2 CAIBE (the most troughly studied system). For Si-Ar^+/Cl_2 CAIBE [1] it was found that the emitted particles mass spectra, under steady state condition, deviate substantially from $SiCl_4$ gas evacking spectrum and from spectrum obtained when $SiCl_4$ target is bombarded with Ar^+ ion beam [11]:

* the dominant species detected are Si, Cl, SiCl, $SiCl_2$ and Ar;

** SiCl radicals are emitted as such as reaction product [12] (not from evacking of $SiCl_4$).

This suggest that the Ar^+ ion beam not only assists removal of target material and reaction

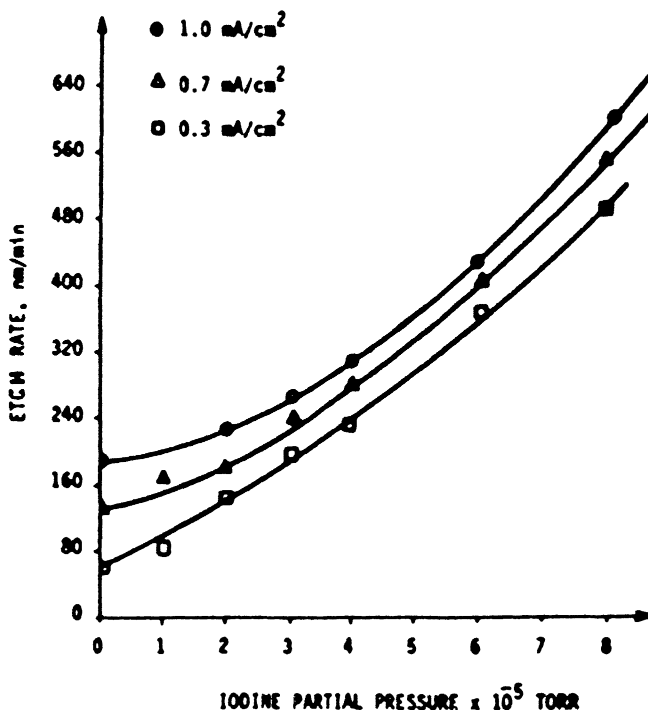

Fig. 3. — Effect of Iodine Partial Pressure on the Etching Rate of Silicon at Different Ion Beam Current Densities and at a constant Ar^+ Ion Beam Energy of 4 keV.

product but brings out changes in reaction between Si and Cl_2. According to Dieleman *et al.* [13] and Mayer *et al.* [14-15], the role of ion bombardment is to weaken the surface target by mixing the absorbed reactive species into the top atomic layers. Thus the surface escape barrier is lowered (because target-target atom bonds are partly replaced by weak target-rectant bonds) and volatil molecular fragments are produced.

Figure 4 present opticals micrographs from (111) plane view samples prepared by Ar^+ IBE (Fig. 4a) and by Ar^+/I_2 CAIBE (Fig. 4b).

In both cases, ion beam conditions are identical and the etching process was stopped at the same step (same hole area) for a convincing comparison. It is clearly shown that the reactive flux of iodine induces a strong increasing from the transparent area (about $1mm^2$ in Fig. 4b) and so from areas of interest in TEM. Similar results were obtained on both plane view and cross-sectional silicon samples prepared by Ar^+/I_2 CAIBE. The eccentric position of the transparent area in figure 4b is certainly related to an inaccurate ion beam alignent, also visible in figure 4a as the hole eccentricity. Moreover, when iodine vapours are used, the hole does not appear at the center of the transparent area (see Fig. 4b). This suggests that a strong dispersion from the incident ion beam occurs during its crossing through the gazeous iodine. Indeed, during this crossing the Gaussian ion current density distribution is strongly altered. This results in the spreading of the etched area (and so from the transparent area) and in the displacement from the hole position which then strongly depends from thickness variations due to the mechanical polishing. So, different holes can appear separately (a second hole is visible in Fig. 4b) at the different places where the intial thickness is minimum.

Figure 5 presents a HREM image of a Si(111) cross-sectional sample prepared by Ar^+/I_2

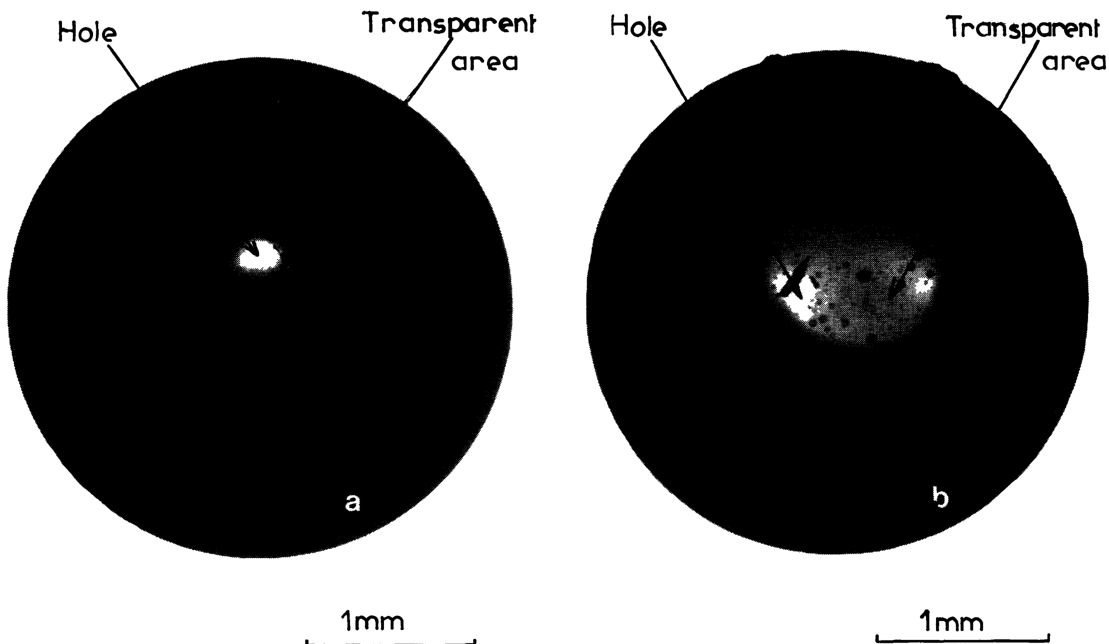

Fig. 4. — Transmission Optical images from (111) plane view silicon samples prepared by: a) Ar^+ IBE: Ion energy = 4 keV, Ion current density = $0.7 mA.cm^{-2}$, Ion beamm incidence = 17°. b) Ar^+/I_2 CAIBE: Identical ion beam conditions, Iodine partial pressure = 10^{-5} Torr.

CAIBE. The crossed lattice fringes characteristic of the crystalline material appear everywhere, suggesting that no artefact is introduced during the preparation of the specimen. The distance between two adjacent (111) planes is 0.314 nm and the image presents a slight modulation of the contrast due to slight thickness variations.

4. Conclusion.

We have demonstrated the interest of chemically assisted ion beam etching (CAIBE) for TEM specimen preparation. When a iodine flux is combined with the Ar^+ ion beam, the thinning rate of silicon samples is strongly increased (up to 4 times in comparison with only Ar^+ ion beam) and the electron transparent area is strongly extended. The technique is simple and can be easily adaptable on a normal inert ion beam thinner. CAIBE has distinct advantages over IBE and RIBE in terms of independent control of etching parameters and no reactive gas is used in the ion source. The Ar^+/I_2 CAIBE can find application for pattern etching on silicon for miroelectronics device fabrication. CAIBE can be a good answer to solve the problem of differential thinning rates obtained with inert ion beam in preparation of TEM specimen from compound and multilayer specimens. There is wide scope to explore the other reactive gases e.g. Cl_2, CF_4, C_2F_6, O_2, S_2F_6 etc. for preparation of TEM specimen.

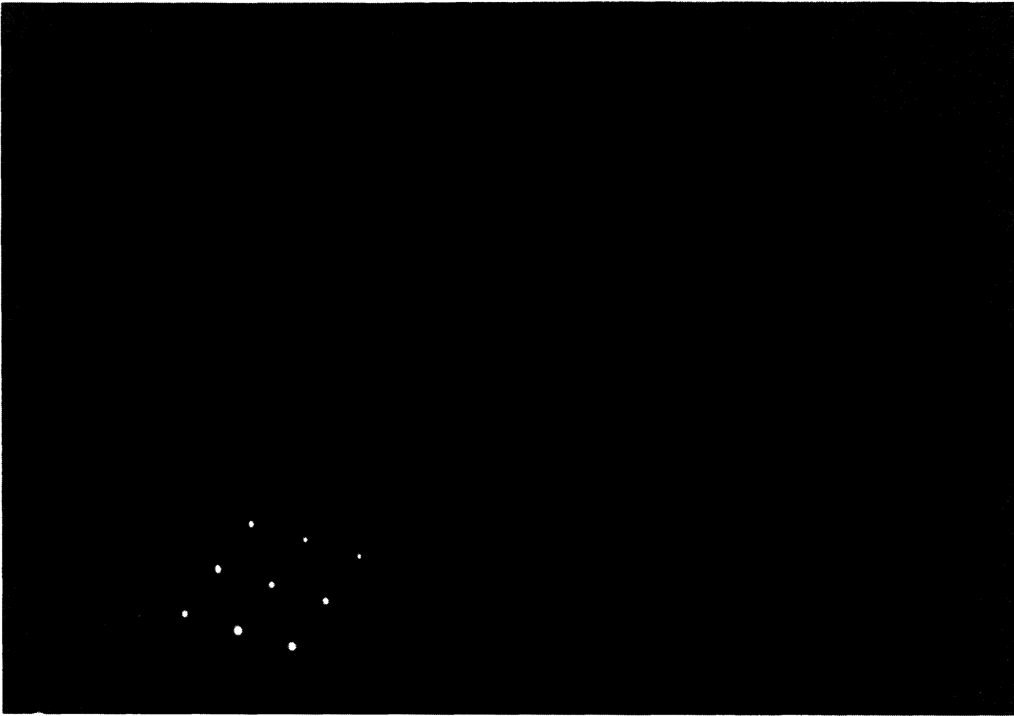

Fig. 5. — High Resolution Transmission Electron Microscopy image (along the <110> direction) of (111) silicon cross-section thinned by Ar^+/I_2 CAIBE

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