Fabrication of X-Ray Masks Using the Silicon Direct Write Electron-Beam Lithography Process and Complementary Electron-Sensitive Resists

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In order to meet the long term goals of the International Technology Roadmap for Semiconductors, it is important to demonstrate that X-ray masks can be fabricated at resolutions well below the 100 nm barrier. This paper presents results on the use of conventional electron-sensitive resists and the silicide direct write electron beam lithography process (SiDWEL) for the fabrication of X-ray masks with sub-100 nm resolution. By optimizing the deposition of the thin films using conventional evaporators, the SiDWEL process was able to achieve linewidths of less than 40 nm and line spacing of less than 100 nm. The silicide patterns formed by the SiDWEL process are sufficiently resistant to plasma etching to directly transfer the patterns to the tantalum absorber. To improve the turnover time for mask fabrication, different writing schemes were studied, including combining the SiDWEL process with QSR-4, a novel negative resist designed specifically for this application. [DOI: 10.1143/JJAP.41.4122]

KEYWORDS: X-ray lithography, mask, electron beam lithography, SiDWEL, resist, etching

1. Introduction

In the semiconductor industry evaluation of different lithographic techniques for the fabrication of sub-100 nm integrated circuits, one important issue is the extendibility of these techniques over several nodes of the International Technology Roadmap for Semiconductors (ITRS).\(^1\) One of the contenders for next-generation lithography (NGL) is proximity X-ray lithography (PXL). This lithographic technique has already demonstrated its capabilities for the 130 nm and 100 nm nodes.\(^2\) However, an important issue related to this technique is the fabrication of masks for sub-100 nm and sub-70 nm resolutions. The absence of a reduction factor in PXL appears as a limiting factor for this technology if no solution can be found to fabricate masks with such resolution. Although sufficient progress has been made in regard to the image placement on the masks for such resolutions,\(^3\) difficulties related to the image transfer remain a key issue. To achieve good contrast with a PXL mask, it is necessary to have at least a thickness in the order of 300 nm of tantalum or tantalum silicide. These materials were chosen not only for their good absorption of X-rays, but also for their chemical stability which makes them suitable for industrial applications.\(^4\) In order to achieve such resolution, there are stringent constraints on the verticality of the etch that is used to transfer the pattern from the electron-sensitive resist layer to the absorber. Such verticality can only be achieved by the use of reactive ion etching (RIE) or a derivative technique such as inductively coupled plasma (ICP). The downfall of these etching techniques is the rapid wear of the electron-sensitive resists under the etching conditions. This kind of wear is typical of organic resists in a plasma chamber. One solution is to use a pattern transfer hard mask, such as SiON, from which the pattern is transferred to the absorber region.\(^5\) This double etching scheme is nevertheless limited by the resolution of the resist patterning.

This paper presents results on the use of conventional electron-sensitive resists combined with the silicide direct write electron beam lithography process (SiDWEL) for the fabrication of X-ray masks with sub-100 nm resolution. The compatibility of the masks fabricated with monolithic microwave integrated circuits (MMIC) applications is discussed. An important aspect of the SiDWEL process is that lines with resolution better than 50 nm have already been demonstrated.\(^6\) At present, the writing speed of the SiDWEL process is a limiting factor for its use in the fabrication of ULSI circuits and other patterns requiring large areas of absorber on the masks. In order to address the issues related to these large areas, a hybrid lithographic process is presented which is a combination of the use of a conventional negative resist and the SiDWEL process. The conventional resist is mainly used for the low-resolution elements (> 250 nm) of the patterns, while the SiDWEL process is used to achieve higher resolution. QSR-4, an in-house negative resist, is used for this purpose since this resist does not need to be spin coated, and therefore can be used on thin membranes without risk of damaging the membrane or introducing stress which in turn can cause errors in the image placement. In this proof-of-concept experiment, stitching of the two patterns (large structures exposed using QSR-4, fine structures exposed using SiDWEL) was achieved using standard alignment techniques for electron beam lithography, using both translation vectors and transfer matrix in exposure position calculations. Demonstrations of both hybrid and SiDWEL patterns are presented.

2. Preparation of the Mask Blank

Membranes used for X-ray lithography are usually made of SiN, SiC, or diamond.\(^7\) In the case of this demonstration, SiN was chosen for its availability. Being the most mechanically fragile of the above membrane materials, it is important to note that these processes demonstrated on SiN are compatible with SiC or diamond membranes without any change in processing. A low-pressure chemical vapor deposition (LPCVD) of silicon nitride was performed on a clean 7.5 cm Si (100) wafer using a dichoro silane:ammonia (5 : 1) mixture at a temperature of 850°C. Such conditions are used to form silicon nitride layers with low internal tensile stress, in order to obtain flat membranes. Back etching of the Si wafer to open the membrane windows was performed using a KOH solution at

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80°C for 20 hours. Membranes were fabricated with layers of LPCVD silicon nitride as thin as 300 nm, with dimensions up to 1 cm². For demonstration purposes, such nitride layers were also used as a substrate for small samples.

Using high pressure conditions (30 mTorr) in an Ar sputtering system, 50 nm of Cr followed by 300 nm of Ta was deposited on membranes without causing any breakage of the 16 membranes used. These results are comparable to those obtained by other groups that studied Ta deposition for X-ray masks. Ta was chosen as the absorber for its chemical stability, which makes masks suitable for cleaning using oxo-acids and strong solvents. Cr is an etch stop barrier for the fluorine based plasma etching used to transfer the pattern to Ta. The grain size for the β-Ta sputtered under these conditions is less than 50 nm. Different deposition techniques were studied for the deposition of the Si and Ni thin films on top of the absorber layers. In order to achieve the maximum resolution for the SiDWEL process, it is important to minimize the energy of incident atoms as they are deposited over the Ta absorber layer in order to reduce the grain size of the Ni layer. The deposition of Ni atoms is usually considered to be carried out by a two-stage mechanism, in which incident (impinging) atoms are initially adsorbed at the surface of the substrate to form a mobile layer, and then migrate over the surface to points where they are incorporated into the lattice. In the first stage of adsorption, incident atoms are physisorbed onto the surface of the substrate, while the second stage in which they are in thermal equilibrium with the substrate corresponds to dissociative chemisorption. While in the physisorbed state, the atoms are not yet in thermal equilibrium with the substrate. The behavior of physisorbed atoms can be described by a conventional diffusion law, as expressed in eq. (1):

\[ \frac{\partial P}{\partial t} = D_0 e^{-E_m/E_b} \nabla^2 P \]  

where \( P \) is the probability of an atom of being at a given position at a given time, \( D_0 \) is a diffusion constant, \( E_m \) is the energy of the barrier from one site to another, and \( E_b \) is the energy of the physisorbed atom. As the atoms have a greater binding energy at the edge of grains, the energy barrier \( E_m \) will be higher for these sites. From eq. (1), it can be inferred that an incident atom with a high energy will have greater probability of diffusion from site to site until it falls into a site at the edge of a grain where it will likely stop, due to the greater binding energy. An incident atom at a high energy will therefore have a greater probability of attaching to an existing grain. This will in turn produce larger grain sizes.

Although sputtering is widely used in the semiconductor industry for high quality thin film deposition, the high energy of incident atoms causes the formation of large grains that limit the resolution of the SiDWEL process and also causes parasitic silicide formation in the unexposed regions. In the case of deposition by Ar sputtering, grain sizes of ~75 nm were observed for Ni layers. Therefore, Joule effect evaporation was chosen instead in order to minimize the energy of the deposited atoms. The pressure during deposition in the evaporator is 10⁻⁶ Torr. Joule effect evaporation allowed the deposition of the Ni layer with an average grain size of less than 20 nm. The silicon and nickel layers deposited over the Ta absorber by Joule effect evaporation were 15 nm in thickness for all samples. While no resist is needed when using solely the SiDWEL process, the samples used to demonstrate the hybrid resist/SiDWEL process were coated with QSR-4 on top of the Si and Ni layers.

3. Lithography by SiDWEL Exposure and Pattern Transfer into Ta Absorber

In the SiDWEL process, a nickel thin film is alloyed with an underlying silicon thin film by a highly focused low-energy (1 keV to 3 keV) electron beam to form etch-resistant silicide patterns, as illustrated in Fig. 1(a). Since the initial nickel layer thickness is less than 20 nm, an excellent resolution can be achieved by this patterning process. Also, these silicide structures are excellent etch masks for fluor-based plasma etching, and therefore a hard mask for the pattern transfer to Ta is unnecessary.

Electron beam lithography for the SiDWEL process was performed on several samples and on a membrane using a modified LEO-1530 FEG scanning electron microscope, externally controlled by means of a vector scan type software. Exposure was carried out on 200 µm square fields. Stitching of several fields of patterns was performed using a precision X–Y stage with a placement accuracy better than 150 nm. Both single and multipass exposure schemes were used for patterning. Exposure tests determined that single pass exposure required a longer exposure time by a factor of 2.4 than a 5-pass writing scheme. In fact, a multipass writing scheme significantly reduces the amount of carbon contamination on the surface. With low-energy processes such as SiDWEL, part of
the electron beam energy is absorbed in this carbon contamination thin film. By reducing the amount of carbon contamination with a multipass writing scheme, there is a significant increase in the effective energy absorbed in the SiDWEL layer. A detailed study of this effect has been reported previously. On the other hand, a small drift in image placement occurs in the elapsed time between each pass. This drift limits the linewidth that can be achieved with the equipment used here to $\sim 100$ nm. Patterns were written with a beam energy of 1.6 keV, and a beam current of 50 pA. After exposure, wet etch of the SiDWEL layers was performed using a HNO$_3$:CH$_3$CHOHCH$_3$:H$_2$O solution to remove the Ni layer, and a HF:NH$_4$F:H$_2$O solution to remove the Si layer, as illustrated in Fig. 1(b). Figure 2 shows a pattern of 175 nm lines fabricated under single pass writing conditions, each separated by 95 nm. This pattern was used to determine that the line edge roughness was of $3\sigma \sim 20$ nm. This line edge roughness is equal to the grain size of the Ni and Si layers. This is in accordance to wet etching models that predict that usually, grain boundaries are etched more rapidly than the grains themselves. Chemical reactions along the boundaries of grains will cut them out, thus removing entire grains and creating notches on the silicide line. Figure 3 shows a pattern with 32-nm-wide lines. Due to the roughness which is on the order of half the linewidth, these lines are not perfectly continuous. An improvement of the grain size should reduce the roughness of the line and give complete continuity.

The silicide structures formed by the SiDWEL process have an excellent chemical selectivity over Ta in a fluorine-based reactive plasma. Using CF$_4$ or SF$_6$ as main etching gases, a selectivity better than 17 between nickel silicide and Ta was measured. Therefore a 30-nm-thick silicide layer can provide an effective etch mask for up to 500 nm of Ta without losing any of the patterns due to wear during etching. A SF$_6$:CH$_4$ mixture was chosen to transfer the electron beam lithography patterns to the Ta absorber layer in a March CS1701 reactive ion etching system (RIE), as illustrated in Fig. 1(c). Etching was performed at low power, 80 W, to avoid heating the membrane which might cause fracture in the nitride. Figure 4 shows patterns etched under these conditions. On the micrograph, lines ranging from 250 nm to 70 nm (nominal width) are visible. All the silicide patterns remain undamaged on top of the Ta layer, demonstrating the excellent chemical resistance of silicide to plasma etching. Figure 5 is a micrograph of a magnified view of a similar line. The verticality of the etched pattern was better than 75°. Although this is not sufficient for ULSI applications of X-ray lithography, it is comparable to results recently obtained by other groups using SiON hard etch masks.

4. Lithography by Hybrid Process

The SiDWEL process has an excellent resolution for X-ray mask application, as demonstrated in the previous section. To
increase the writing speed for a large mask while still maintaining the high resolution of the process, one solution is to combine it with the use of a conventional resist by writing the large elements of the pattern with the resist and high resolution elements with the SiDWEL process. An important issue in combining a resist with the SiDWEL process is that heating the samples above 100°C will cause parasite silicide dots to form at the nickel-silicon interface. These dots would be transferred during the RIE etching to the Ta absorber, hence creating defects in the mask. One of the criteria in choosing the resist is therefore to avoid any post-lithography baking. Also, a negative resist facilitates the treatment of the pattern data prior to exposure. With SiDWEL process being negative, a positive resist would require the inversion of the elements that would be exposed by the resist. Such an inversion, although possible, would be difficult due to the need of creating overlaps between the different elements of the patterns. Finally, for similar reasons, it is preferable to have a resist that can be exposed under similar conditions as the SiDWEL process. QSR-4 is a negative resist developed in-house that is efficient at low electron beam energy. At 3 keV, the threshold dose is on the order of 500 µC/cm², which does not qualify this resist for direct-write applications, but is sufficient for mask fabrication. No bake of the resist is necessary after exposure. The samples used to demonstrate the hybrid process were coated with QSR-4 using two different spreading techniques: spin coating and dipping. QSR-4 allowed the use of both spreading techniques and gave similar results in both cases. However, dipping is the chosen spreading method in order to limit the mechanical stress on the membranes and avoid fracturing of the membrane material. Lithography was performed using a JEOL-6300 SEM using the same external vector scan software as was used for SiDWEL lithography. The exposure current was 100 pA at 3 keV. Rough patterning was performed, exposing lines 250 nm wide and larger. The sample was then developed using CH₃CHOHCH₂. This type of development leaves the underlying Ni layer undamaged. A second round of exposure is then carried out in the same lithography system for the SiDWEL process. In order to stitch together the SiDWEL elements of the patterns with the previous elements, an alignment is made using a four-element transfer matrix and a translation vector. The SiDWEL exposure is carried out at 3 keV to expose pattern elements of nominal widths from 100 to 250 nm. After this second exposure, the unexposed regions of the Ni layer are etched using a HNO₃:CH₃CHOHCH₂:H₂O solution. Regions that are underneath the QSR-4 patterns or that have been transformed into silicide by the SiDWEL process are not affected by etching. The silicon layer is subsequently etched using a HF:NH₄F:H₂O solution. Once again, regions protected by QSR-4 patterns or transformed into silicide are unaffected by the etching. Plasma etching is performed using the same parameters as were used for the patterns exposed solely with the SiDWEL process. Figure 6 shows results of the hybrid process, where the wide line is exposed using QSR-4 and the smaller lines by SiDWEL. The pattern was transferred down to the Cr layer without damaging either the nickel patterned using the resist or the silicidic structures. Similar patterns were achieved with QSR-4 elements as small as 250 nm, as shown in Fig. 7. Defects and line edge roughness are visible on the smaller QSR-4 lines. They can be mainly attributed to defects in the initial material used in the preparation of QSR-4 and could be eliminated by a filtering procedure prior to coating. Another cause of line edge roughness is the etch solution of the nickel layer which still needs to be optimized. An image placement accuracy better than 200 nm was measured. This could be improved using a higher precision stage and a better software for alignment data.

5. Conclusions

It has been demonstrated that the SiDWEL process is suitable for the fabrication of etch masks for pattern transfer to Ta absorber layers, with linewidths as narrow as 32 nm. The resolution and the line edge roughness is mainly limited by the grain size of the Ni and Si layers used in silicide formation. The line edge roughness can therefore be reduced by improving the deposition techniques in order to reduce the energy of the incident atoms during deposition. Improvement of the writing speed allows the writing of more than 1 m in gate length on a single mask using only the SiDWEL process. This satisfies requirements for most microwave monolithic integrated circuit gate masks. Nevertheless, work remains to be done to achieve ULSI writing length on a mask using this technique. An interesting approach consists of the
combination of the SiDWEL process with a negative resist in a hybrid exposure scheme. Such an exposure scheme was demonstrated, using QSR-4, an in-house negative resist that can be spin coated or dip coated. The dip coating solution has the advantage of preventing stress on the membrane, which can introduce image placement errors as well as fracture in the membrane material. The dip coating scheme produces a uniform thin resist layer that can be deposited on top of the SiDWEL thin films (Ni and Si layers). Moreover, lithography can be carried out for both the negative resist and SiDWEL using the same exposure parameters, thus improving the stitching of the two elements of the patterns: QSR-4 was used to pattern lines 250 nm and larger, while the SiDWEL process was used for sub-200 nm lines. It was demonstrated that QSR-4 adequately protects the underlying Ni during the wet etching of the Ni thin film for removing the unexposed areas. Once the Ni etch was complete, it was also demonstrated that both types of structures, Ni protected by the resist and silicide structures formed by SiDWEL, were able to be used to transfer the pattern to the 300-nm-thick underlying Ta absorber. In order to achieve good stitching of the patterns, it was necessary to do an alignment procedure using a four-value transfer matrix and a translation vector to obtain a 200 nm image placement accuracy. Further work remains to be performed in order to achieve alignment with an accuracy compatible with ULSI requirements. With the resolution of the SiDWEL process being only limited by the grain size, the results presented here might indicate a method for extending the proximity X-ray technology down to sub-70 nm nodes of integrated circuit fabrication.