行政院國家科學委員會專題研究計畫  期中進度報告

X-ray 及電子束 (e-beam) 直接微影技術在多層導體連線上的
應用研究

計畫類別：個別型計畫
計畫編號：NSC93-2215-E-009-035-
執行期間：93年08月01日至94年07月31日
執行單位：國立交通大學電子工程學系暨電子研究所

計畫主持人：施敏
共同主持人：張鼎張
計畫參與人員：陳紀文、王敏全、楊富明

報告類型：精簡報告
報告附件：出席國際會議研究心得報告及發表論文
處理方式：本計畫可公開查詢

中華民國94年5月31日
行政院國家科學委員會補助專題研究計畫期中報告

X-ray 及電子束(e-beam)直接微影技術在多層導體連線上的應用研究(1/2)

Study on X-ray and E-beam Direct Patterning Technology for Multilevel Interconnect Applications

計畫編號：NSC 93-2215-E-009-035-
執行期間：93年08月01日至94年07月31日
計畫主持人：施敏 交通大學電子工程學系
計畫參與人員：陳紀文 交通大學電子所
王敏全 清華大學材料所
楊富明 交通大學電子所

一、中文摘要

本計畫將針對 X-ray 及電子束(e-beam)曝光對低介電常數材料進行直接圖形化(direct patterning)技術進行研究：第一年，首先建立最佳的直接圖形化低介電常數材料的曝光參數。此外，銅金屬與經過 X-ray 及 e-beam 曝光後 Low-k 介電薄膜的交互作用也將在這一年內進行研究。在第二年，將運用此技術進行製程整合上的探討，包括 X-ray 及 e-beam 曝光及在顯影後所造成的介電特性穩定與否、抗熱能力、電性可靠度以及與銅金屬化學機械研磨相容性等等。除此之外，我們也將利用 X-ray 與 e-beam 直接圖形化的技術製作銅導線的梳狀測試結構(comb structure)，並且進行共平面(in plane)介電特性、銅導線的電子遷移率可靠性之探討。此外，我們也將製作高頻測試結構進行載子高頻傳輸行為的研究。藉由以上所提的方式深入並廣泛地評估直接圖形化技術在 IC 製程應用上的可行性。

關鍵詞：低介電常數材料，X-ray，電子束，直接圖形化

Abstract

In this project, we propose X-ray and e-beam exposure to direct pattern the low-k dielectric in this study. In first year, we will establish the optimum exposure parameter for the direct patterning of low-k material. Moreover, we also study the interaction of Cu and low-k materials exposed by X-ray and e-beam. In second year, we will investigate the integration issues of this direct patterning technique on low-k material. This issue include the dielectric stability of low-k material after e-beam and X-ray exposure and development process, the thermal resistibility, electrical reliability, and the compatibility with copper CMP process etc. In addition, we also make the Cu comb structure by this technique to do test. Simultaneously, we evaluate the dielectric properties of the inner layer of this structure and the reliability of electromigration for Cu interconnect. Furthermore, we also make high frequency test structure to investigate the carrier transfer
behavior under high frequency operation. Finally, we evaluate the feasibility of this technique during IC manufacture process.

**Keywords**: low-k dielectric, X-ray, e-beam, direct pattern

二、缘由与目的

As the complexity of function of the integrated circuit increases, the space between metal line and metal line become more narrow and longer. The phenomenon will cause the serious RC time delay, then reduce the operation speed of whole integrated circuit. In order to conquer the problem, the Cu metal and low k materials are utilized to replace the traditional Al metal and SiO₂ in semiconductor technology to enhance the IC performance. However, for defining device pattern in general IC manufacture process, we will utilize photoresist to define it. But the low-k dielectric will be degraded during the photoresist removal process. Furthermore, with the decrease of the structure size, the removal of PR is more and more difficult, resulting in the big challenge for pattern transfer step. To overcome this issue, we propose X-ray and e-beam exposure to direct pattern the low-k dielectric in this study. In addition, as the low-k dielectric is integrated with Cu, the dielectric properties will be demoted due to Cu diffusing into low-k materials.

三、实验流程

HSQ resins diluted in methylisobutyl ketone (MIBK) were spun on Si wafers at 2000 rpm for 20 sec to form 400-nm-thick films. After baking at 150 °C on a hot plate for 1 min, the films are cured by X-ray exposure at SRRC. The films were exposed in different dose, including 10, 20, 30, 40, 50, 65W/cm². Then e-beam exposure was carried out overall on as-baked HSQ films with doses ranging from 100 to 700 uC/cm² by use of a Leica Weprint200 stepper. The e-beam energy was 40 KeV with beam size 20 nm. The exposure doses of e-beam irradiation could be determined according to material and electrical analyses. As for the pattern formation of HSQ lines, as-baked HSQ films were irradiated with X-ray and e-beam according to desire pattern layout. We observed the exposed pattern by scanning electron microscope (SEM) image to demonstrate the feasibility of e-beam direct patterning on HSQ films. The chemical structures of all aforementioned samples were characterized by Fourier transform infrared (FTIR Bio-Red QS300) spectroscopy. Electrical measurements were conducted on metal insulator semiconductor (MIS) capacitors. The dielectric constant measurements were conducted using a Keithley Model 82 CV meter. The area of the gate electrode was 0.00503 cm² for C-V analysis. The leakage current (I-V) characteristics were measured using a HP4156 electrical meter.

四、结果与讨论

The X-ray lithography process flow is shown in Figure 1. Materials analysis is measured to evaluate the influence of X-ray exposure on HSQ film. Figure 2 show the FTIR spectra of HSQ films that receive different exposure dose. From the spectra chemical bonding of the buck film shows significant changes in the diagram. At low exposure dose regime, the spectra of HSQ film were almost the same with the only baking film. But with the dose increase, the
spectra change gradually. The Si-O cage-like peak intensities at 1130 cm\(^{-1}\) become stronger, and the net-work peak intensities at 1070 cm\(^{-1}\) become weaker. It shows clearly that the material structure of HSQ changes from cage-like to network. Although the peak intensity is not strong compare with the as-cured film, it is more and more similar to the as-cured film. It means that X-ray indeed affect the HSQ film. Figure 3 shows the pattern of HSQ after X-ray exposure by SEM. Figure 4 shows comparison of dielectric constants of X-ray as-exposed HSQ with and without thermal annealing. Figure 5 shows the leakage current density of HSQ films with different X-ray exposure doses after thermal annealing in a furnace at 400 °C for 1 hour. It is found that the leakage current density of X-ray exposed films after furnace annealing is almost close to that of the conventional furnace-curing HSQ. E-beam lithography process for the fabrication of damascene structure is shown in Figure 6. Figure 7 shows the FTIR spectra of HSQ films with different doses of E-beam exposure. In the furnace-cured HSQ, Si-O bending cage-like peak (863 cm\(^{-1}\)), Si-O stretching modes (cage-like at near 1132 cm\(^{-1}\), network-like at near 1072 cm\(^{-1}\)), and Si-H stretching mode (near 2250 cm\(^{-1}\)) are observed. The Si-H group makes the surface hydrophobic and prevents moisture uptake. The low dielectric properties of HSQ film can be achieved if the density of Si-H bonding is maintained at a high level. After e-beam exposure, the peak of Si-O stretching vibration and that of bending vibration significantly change. E-beam exposure provides the as-baked HSQ film energy to be cross-linked and transfer the HSQ from cage-like structure to network-like one. It clearly shows the intensity of Si-O network mode grows at the expense of the intensity of Si-O cage-like mode with increasing e-beam exposure doses. In addition, the intensity of Si-H stretching mode is slightly decreased with increasing e-beam exposure doses. This indicates the structure of the HSQ film changes from the cage-like to a stable three-dimensional network structure via the breakage of Si-O cage-like and Si-H bonds, and subsequently forming Si-O-Si network. However, an excess of Si-H bonding breakdown will lead to the generation of dangling bonds in HSQ film, resulting in degraded dielectric properties. Figure 8 shows the leakage current of e-beam exposed HSQ films at different doses. It is observed that the leakage current of e-beam exposed HSQ film with e-beam dosage from 100 uC/cm\(^2\) to 600 uC/cm\(^2\) have the similar values close to that of furnace cured one. Meanwhile, the leakage current of e-beam exposed HSQ with a dose of 400 uC/cm\(^2\) is lower than others. While the exposure dosage exceeds 700 uC/cm\(^2\), the leakage current density of e-beam exposed HSQ will increase one order of magnitude than that of furnace-cured one. The dielectric constant of e-beam as-exposed HSQ films at different doses is shown in Figure 9. The results reveal that the dielectric constant of e-beam as-exposed films with e-beam doses between 100 uC/cm\(^2\) and 600 uC/cm\(^2\) is larger than that of furnace-cured one. Especially, the dielectric constant of e-beam exposed HSQ will increase significantly, as the dose exceeds 700 uC/cm\(^2\). According to aforementioned electrical analyses, the dielectric loss is inferred to be due to the destruction of Si-H functional groups and the adsorption of polarized components in HSQ films after the e-beam exposed dose over than 400 uC/cm\(^2\). The inference can be verified by
the FTIR spectra shown in Figure 7. The intensity of Si-H bonds was found to be smaller than that of furnace-cured HSQ as the e-beam dosage exposed from 400 to 700 uC/cm². This implies that the e-beam dosage cannot be too high to obtain the required dielectric properties of low-k HSQ. In this work, the optimum e-beam exposure dosage was obtained with a dose of 400 uC/cm².

In order to verify the feasibility of e-beam direct patterning on HSQ films, we perform the e-beam exposure according to desired pattern layout with the optimum dose of 400 uC/cm². In some cases, it was found that portions of dense line patterns were collapsed after development processes in an aqueous solution of 2.38 % TMAH, rinsed with water, and dried in a nitrogen blow, as shown in Figure 10. The most likely scenario is that the development process is overtime so that the dense lines become finer. It reduces the sustaining force between patterned HSQ film and Si substrate. Moreover, a capillary force is produced from the surface tension of the rinse solution remaining in the spaces between pattern lines. If the capillary force is larger than the sustaining force during drying process, the pattern collapses will arise after development process (as illustrated in Figure 11). For such a reason, with careful control of drying processes, the image of line patterns with line width of 60 nm can be obtained in our work, as shown in Figure 12. According to the above results, the coverage of HSQ films exposed by e-beam can be cross-linked, while the others without e-beam exposure will be dissolvable in the TMAH aqueous solution and forming trench patterns. Therefore, it demonstrated the feasibility of e-beam direct patterning on HSQ films.

五、成果自評

We have performed X-ray and e-beam lithography technique to direct pattern the low-k HSQ film. The X-ray exposure can effectively cure HSQ film to make the cage-like bonds transform to network bonds. Then the un-exposed part of HSQ film can be developed by HSQ solvent. In addition, the low-k dielectric characteristics of X-ray as-exposed HSQ films can be enhanced by a thermal annealing process. The smallest size of 60 nm has been demonstrated in e-beam lithography. Such technique does not need the use of photoresist. It is believed that the technique can be incorporated into next generation of interconnect systems as the devices shrink into nano-scale regimes.

六、參考文獻


Figure 1 Scheme of X-ray direct patterning of low-k dielectrics for the manufacture of damascene structure. Step I: X-ray illumination on HSQ through a mask (line width ~1 µm); Step II: with X-ray illumination, regions I are crossed-linked. Without X-ray illumination, region II was kept gel-like state; step III: After development, region II is dissolved in HSQ solvent and regions I are remained.

Figure 2 FTIR spectra of HSQ films with different X-ray exposure doses.

Figure 3 The optical photo image of HSQ film after X-ray exposure followed by the development with HSQ solvent.
Figure 4 Comparison of dielectric constants of X-ray as-exposed HSQ with and without thermal annealing.

Figure 5 The leakage current density of HSQ film with different X-ray exposure doses after the thermal annealing in furnace at 400 °C for 1 hour.

Figure 6 Proposed e-beam lithography process for the fabrication of damascene structure.

Figure 7 FTIR spectra of HSQ films with different doses of electron beam exposure, ranging from 100 uC/cm² to 700 uC/cm².
Figure 8 The leakage current densities of e-beam exposed HSQ films at different doses.

Figure 9 Dielectric constant of e-beam exposed HSQ films at different doses.

Figure 10 The SEM cross-sectioned profile of collapsed pattern for dense HSQ lines.

Figure 11 The possible scenario of pattern collapse for dense HSQ lines.
Figure 12 The SEM micrograph of patterned HSQ film with critical dimensions of 60 nm.