

Sub-100 nm Nanolithography and Pattern Transfer on Compound Semiconductor Using Sol-Gel-Derived TiO₂ Resist

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Typical methods for sub-100 nm compound semiconductor patterning are based on indirect pattern transfer using SiO₂ or SiN₄ as intermediate masks, which inevitably increase the complexity of pattern transfer and cause potential damage to samples. We present an approach of direct pattern transfer using Ti(OBuⁿ)₄ sol-gel-derived TiO₂ resist as mask. The optimal dose of TiO₂ resist for E-beam lithography is ~220 mC/cm². The sample InP compound semiconductor etching selectivity to TiO₂ resist is as high as 9:1 with aspect ratio of over 30:1. Various sub-100 nm scale inductively coupled plasma etching patterns are obtained with a high-quality etching profile. The smallest feature is as small as 20 nm wide with a depth of over 600 nm. © 2008 The Electrochemical Society. [DOI: 10.1149/1.2883730] All rights reserved.

Manuscript submitted November 28, 2007; revised manuscript received January 8, 2008. Available electronically March 11, 2008.

Compound semiconductor-based devices have a variety of applications in communications, photonics, and optoelectronics, such as transistors, lasers, diodes, photodetectors, etc. Recently, semiconductor devices with a sub-100 nm scale have been drawing more and more attention due to their high integratability and various unique applications, such as very-large-scale integration, quantum disk confinement structure, and photonic bandgap.¹⁻⁴ For those purposes, various instruments and techniques have been developed to reduce the size of compound semiconductor devices to such a small scale.

However, currently sub-100 nm patterning of a compound semiconductor is limited by the lithography resist. For example, for InP semiconductor compound etching, the etching selectivity of poly(methyl methacrylate) (PMMA) is as low as 2-5.5 In addition, PMMA could not resist high temperatures over 200°C, which is required by chlorine-based InP dry etching to remove the by-product during the etching process. Hence, SiO₂ or SiN₄ are typically used as intermediate masks for indirect pattern transfer. First, nanopatterns are formed on resist using nanolithography. Next, the patterns are transferred to SiO₂ or SiN₄ by dry etching. Finally, after removing the resist and subsequent pattern transfer to the compound semiconductor by etching using intermediate SiO₂ or SiN₄ mask, this intermediate mask has to be removed for the subsequent fabrication process. These additional mask transfer and etching away processes inevitably increase the complexity of InP submicrometer patterning, especially for sub-100 nm size patterns. Therefore, it is desirable to find an easier and effective method of compound semiconductor pattern transfer. One method is to use the recently reported metal oxide nanolithography resist,⁶⁻⁸ which is expected to have harder structures and higher resistance to temperature and etching chemicals.

In this paper, we present a method of sub-100 nm direct pattern transfer of compound semiconductor using sol-gel-derived spincoatable TiO₂ resist as mask. Here, we specifically demonstrate the technique on InP compound semiconductor using inductively coupled plasma reactive ion etching (ICP-RIE). This technique can be readily extended to GaAs, InGaAs, InGaP, InAlAs, AlGaAs, InGaAsP, and other compound semiconductors with similar etching chemistry. Using spin-coated TiO₂ as mask, we show that 20 nm direct pattern transfer with high selectivity and high aspect ratio etching profile can be obtained.

Experimental

Resist making and characterization.— Titanium *n*-butoxide was used to make sol-gel-derived spin-coatable TiO_2 resist, which could be used in both photolithography and E-beam lithography applications. Benzonyl acetone (BzAc) was used to stabilize titanium

n-butoxide. They reacted in ethanol solvent with an equal molar amount. All reactions were carried out inside a glove box (<14% relative humidity) for 3 h at room temperature. The solution was clear and no precipitation was observed. Then the solution was filtered through a 0.2 μ m filter to remove large particles and improve the resist spin-coating quality. The desired thickness was obtained by varying the spin rate and dilution ratio using 1-petonal. A Woollam variable angle spectroscopic ellipsometer and atomic force microscope were used for resist thickness measurement.

Due to the vulnerability of the titanium atom in $Ti(OBu^n)_4$ to nucleophilic attack through the electronegative butoxyl groups, titanium *n*-butoxide shows a fast hydrolysis when exposed to moisture. To protect the titanium atom from the nucleophilic attack, we chelated the $Ti(OBu^n)_4$ with a β -ketoesters chelating agent, BzAc. Figure 1 shows the reaction mechanism of the chelation of $Ti(OBu^n)_4$ with BzAc. Like most β -diketones, BzAc is capable of keto-enol tautomerism. When $Ti(OBu^n)_4$ is present, the enol form BzAc can easily react with it and form a chelated compound, which is more stable due to the steric hindrance effect. As a result, hydrophilicity of titanium *n*-butoxide is significantly reduced.

A Thermo Nicolet Nexus 870 FT-IR spectrometer was used to study the chemical bonds, atmospheric stability, and thermal properties of BzAc-stabilized TiO₂ sol-gel. Figure 2 shows the Fourier transform infrared (FTIR) spectrum of the as-spin-coated (at 0 h) TiO₂ resist. Two primary absorption peaks at 1593 and 1511 cm⁻¹ were attributed to v(C=O) and v(C=C) vibrations of the chelate ring formed between the Ti core and BzAc, respectively, which indicates the formation of the expected chelate complex. The TiO₂ film obtained was then exposed to the atmosphere (25°C, 30% humidity) for different time durations and then characterized by FTIR spectra to study the air stability. The absorption peaks corresponding to v(C=C) and v(C=C) were almost unchanged even after 48 h, which indicated a high environmental stability of the chelated TiO₂ sol-gel and showed that the chelate ring of Ti and BzAc can effectively stabilize the TiO₂ sol-gel-derived resist.

The influence of prelithography baking temperature on TiO2 re-



Figure 1. Reaction mechanism of BzAc with Ti(OBuⁿ)₄.

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Figure 2. FTIR absorption spectra of spin-coated ${\rm TiO}_2$ resist after different lengths of time.

sist was studied using AXIC JetFirst 150 rapid temperature processing (RTP) system and FTIR spectra measurements. The baking temperature varied from 100 to 700°C with increments of 100°C for 5 min, respectively. As shown in Fig. 3, the FTIR spectra indicate that when the baking temperature goes up to 300°C, the absorption peaks corresponding to vibrations of the chelate ring have almost no change, which indicates a good thermal stability of the TiO₂ resist. This good thermal stability gives the derived TiO₂ resist more applications than conventional lithography resists in semiconductor device fabrications. When the temperature goes above 400°C, the absorption peaks corresponding to vibrations of the chelate ring start to decrease and eventually disappear above 500°C, which means the chelate rings are all broken down. When the temperature goes above 600°C, pure TiO₂ metal oxide is formed.

Nanolithography.— The 100 kV high-resolution Leica VB6-HR E-beam lithography system was used to study the dose characteristics of TiO_2 resist at a 5 nA beam current, and sub-100 nm nanolithography was performed using the JEOL JBX-9300FS electron beam lithography system at 100 kV with 2 nA beam current. Patterned resist was developed in acetone and rinsed in isopropyl alcohol (IPA) for 10 s. Zeiss ultrahigh-resolution field-emission scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the high-resolution TiO_2 patterns.

Before being transferred to E-beam writing, the TiO_2 spin-coated sample wafers were soft-baked at 80°C for 30 min. The measured



Figure 3. FTIR absorption spectra of spin-coated TiO_2 resist under different prelithography baking temperatures.



Figure 4. Developed TiO_2 E-beam lithography pattern with dose of 219 mC/cm²; feature size is 20 nm.

thickness of TiO₂ resist was ~300 nm. The E-beam writing dose ranged from 40 to 900 mC/cm² to study the exposure characteristics of TiO₂ resist. The dose of ~220 mC/cm² showed an overall good lithography quality. Finally, a dose range from 100 to 500 mC/cm² was used for this study. As shown in Fig. 4, the TiO₂ lithography pattern with the exposure doses of 219 mC/cm² showed a good profile quality and development properties.

ICP-RIE etching.— To study the thermal characteristics and performance of TiO_2 resist patterns as an etching mask, the patterned sample InP compounds were transferred to the AXIC JetFirst 150 RTP system again for postlithography annealing. The postannealing temperature varied from 200 to 500°C with an increment of 100°C.

Typically, two chemistries were used for InP compound patterning by dry etching, chlorine-based etching, and methane-based etching. The former provided a high etching speed over 1 μ m/min. The latter provided a lower etching rate of 50–100 nm/min with polymer by-products, which is good for shallow etching with good depth control. Various instruments are generally used for dry etching, including RIE,⁹ chemically assisted ion beam etching,¹⁰ electron cyclotron resonance-reactive ion beam etching,¹¹ and ICP-RIE.¹²⁻¹⁵ Among them, ICP-RIE is most intensively studied due to its capability of obtaining a high etching rate and low physical damage to etching samples at the same time. Hence, chlorine-based ICP-RIE is utilized to study the direct pattern transfer using TiO₂ as a mask.

In this study, a PlasmTherm SLR 770 ICP-RIE system was used for TiO₂ pattern transfer. The coil power was set at 800 W for a relatively fast etching speed. The physical etching by etching radicals and undercut of the profile primarily depended on radio frequency (rf) power. The increased rf power improved the anisotropy, whereas it decreased the etching selectivity. Therefore, an optimal rf power of 120 W was used to balance the undercut and etching selectivity. The anisotropy of dry etching greatly depended on ICP chamber pressure;^{16,17} thus, 1.7 mTorr was used for chamber pressure to optimize etching anisotropy after calibration tests. The byproduct of chlorine-based InP ICP etching was InCl_x, which was generally involatile below 150°C. In the study, we used an elevated substrate temperature of 250°C to remove etching product, improve the etching rate, and smooth the surface. In addition to standard Cl₂/Ar gas mixture, H₂ was added to the etching chamber to balance the physical and chemical processes. An optimal Cl₂/Ar/H₂ ratio range from 2/3/1.5 to 2/3/2.5 was chosen for etching due to its best overall etching profile. In this range, almost all Cl₂ reacted with H₂ in the etching chamber, resulting in the smallest amount of radicals responsible for chemical etching and, therefore the etching was bal-



Figure 5. InP compound etching control sample under optimal etching conditions by ICP-RIE.

anced by Ar physical etching. Figure 5 shows the control sample for InP compound semiconductor etching under optimal etching conditions.

TiO₂ patterned sample wafers were then etched using the above optimal conditions. Figure 6 shows the selectivity of sample InP compound semiconductor to TiO₂ spin-coatable resists at different postlithography annealing temperatures. The selectivity increased from 2 to \sim 9 when the annealing temperature was increased from 200 to 300°C, remained at 9 until 400°C, and dropped to 2 at 500°C. The increase in etching selectivity after the postannealing processes was primarily due to the formation of pure metal oxide. High-temperature annealing breaks down chelate rings in stabilized TiO₂ resist and causes crystallization of TiO₂ resist to pure metal oxide, which is known to have a much harder structure and higher resistance to chlorine-based etching chemicals. This process increased the etching selectivity with the increase of TiO₂ postannealing temperature. As a result, the etching selectivity was increased from 2 to 9 and kept at 9 when the annealing temperature was increased from 200 to 400°C. The possible reason for the drop in etching selectivity after 400°C was the thermal decomposition of bulk InP surfaces at temperatures over ~ 480 °C.^{18,19} Here, the decomposition temperature shift from 480 to 400°C could be due to



Figure 6. Selectivity of InP to TiO_2 spin-coatable resist at different postannealing temperatures.



Figure 7. ICP-RIE etching using sol-gel-derived TiO_2 resist as a mask. (a) SEM pictures of 100 nm diameter pillars etched by ICP-RIE. (b) SEM pictures of 40 nm wide grid etching pattern; etching depth is over 1200 nm. (c) SEM pictures of grid-shaped etching patterns. The line is as small as 20 nm wide and over 600 nm deep.

the fast heating rate of 500° C/min in RTP processing, which has up to 15% overheating when the annealing temperature arrives at the preset temperature. As a result, the actual temperature experienced by the TiO₂ resist coated InP wafer at the beginning would be tens of degrees higher than the preset temperature. During the thermal decomposition of InP surface at high temperatures, many macroscopic etch pits are formed, which degraded the subsequent etching process due to the macromasking effect. In addition, due to P depletion and In accumulation on the InP surface during decomposition, the chemical etching in ICP etching was affected, which led to a decrease of etching selectivity as well.

As shown in Fig. 7, we achieved various sub-100 nm dry-etching patterns of InP compound semiconductor with good profile quality using spin-coated TiO₂ resist as a mask. Figure 7a shows an etching of 100 nm diameter pillars. Figure 7b shows a 40 nm feature etching, where the etching depth is over 1200 nm (aspect ratio > 30:1).

A smooth etching sidewall has been achieved. Figure 7c shows a grid-shape etching pattern, where etching features as small as 20 nm wide and over 600 nm deep (aspect ratio of over 30:1) have been successfully obtained.

Conclusion

We have realized a nanolithography using sol-gel-derived TiO₂ resist and demonstrated its new applications to compound semiconductor direct nanopatterning using TiO2 as a mask. The optimal dose of sol-gel-derived TiO₂ as E-beam lithography resist is \sim 220 mC/cm². A thermal stability study of spin-coated TiO₂ shows good performance as a lithography resist even at 300°C, which will have wider applications than conventional resists. Postlithography annealing at different temperatures is performed to study temperature dependence of patterned TiO₂ resist as a dry-etching mask. The etching selectivity of sample InP compound semiconductor to TiO₂ resist is as high as 9. A variety of sub-100 nm dry-etching patterns have been obtained. SEM pictures show good profile qualities for those nanometer-scale etching patterns, such as a smooth etching sidewall, high aspect ratio of etching patterns, and ultrasmall etching features. The aspect ratio of etching patterns is over 30:1, and the smallest feature is as small as 20 nm and over 600 nm deep. This sol-gel-derived TiO₂ spin-coatable nanolithography resist with high etching selectivity and a high-aspect-ratio etching profile provides a convenient way to directly pattern compound semiconductor material for various challenging nanometer-scale photonic, electronic, and optoelectronic applications.

Acknowledgments

The work was supported by the NSF under award no. ECS-0501589 and ECCS 0622185, by the NSF MRSEC program under grant no. DMR-0520513, by the NASA Institute for Nanoelectronics and Computing under award no. NCC 2-1363, and by the National Center for Learning and Teaching in Nanoscale Science and Engineering (NCLT) under the NSF grant no. 0426328. The work was performed in part at the Cornell NanoScale Facility, a member of the

National Nanotechnology Infrastructure Network, which is supported by the NSF (grant no. ECS-0335765).

Northwestern University assisted in meeting the publication costs of this article.

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