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Residual free reactive ion etching of the Bell contact Ti/Pt/Au

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Abstract

The etching of the complete Bell contact consisting of a layer of Ti/Pt/Au was performed in highly reactive plasmas containing Cl_2 for Ti, PF_3/NF_3 for Pt, and Cl_2 and/or BCl_3 for Au. All the constituents of the Bell contact form volatile compounds in either capacitively-coupled low-density plasmas or high-density plasmas generated by electron cyclotron resonance. This is conditio sine qua non for surfaces and sidewalls which have to remain free of any residues. © 2002 Published by Elsevier Science Ltd.

1. Introduction

For p-contacting on III/V compound semiconductors, variations of the Bell contact Pt/Ti/Pt/Au [1] have evolved to be the most successful. The requirements that a contact has to meet are

1. ohmic contact to the p-doped top region of the semiconductor;
2. good adhesion of this film to surfaces of semiconductor(s) and oxides;
3. ease of bonding, high resistance to corrosion, high elongation to allow thermal expansion mismatch with the substrate;
4. suitability for further high-resolution electroforming.

It is obvious that for these diverging purposes, more than one metal is required. Since the first two qualities can be fulfilled by titanium or chromium, and the last two by gold, which severely degrades the electrical quality of the p^+ zone, we have to add a third metal to serve as a low-ohmic diffusion barrier.

Titanium or chromium are chosen because of

- their high affinity to oxygen, which makes possible even the reduction of silica, by means of which native oxides can be removed and a good interlink at atomic scale is possible;
- their occurrence in many oxidation states from I to IV for Ti and I to VI for Cr, with the dramatic consequence that the oxides of the low oxidation levels Cr^{II}, Ti^{II} or Ti^{III} have fairly good metallic conductivities (in contrast to e.g. Al_2O_3), and
- their extremely good gettering behavior: the detrimental effect of reaction products can be neutralized by interstitial dissolution.

With these metals as contact, the lowest contact resistivities challenge the limits of measuring accuracy which are possible with the transmission line method (TLM) or contact hole [2,3]. However, since no suitable etchants for all three layer components are known, the most usual way is to use a simple lift-off technique. In this case, the metal is plated after a process chain which comprises photoresist processing. Hence, the surface which is going to be metallized is prone to contamination. For columnar vertical cavity surface emitting laser (VCSELs), for which a very low contact resistance is required, a direct metal coating on top of a cleaned semiconductor surface is highly recommended. This, in turn, is synonymous with the demand for perfect etching of the quadruple–metal sandwich. Etching means the residue-free removal, which requires the reproducible generation of volatile compounds. Otherwise, fences will build up at the edges of the photoresist, and these can possibly disintegrate and contaminate the surface

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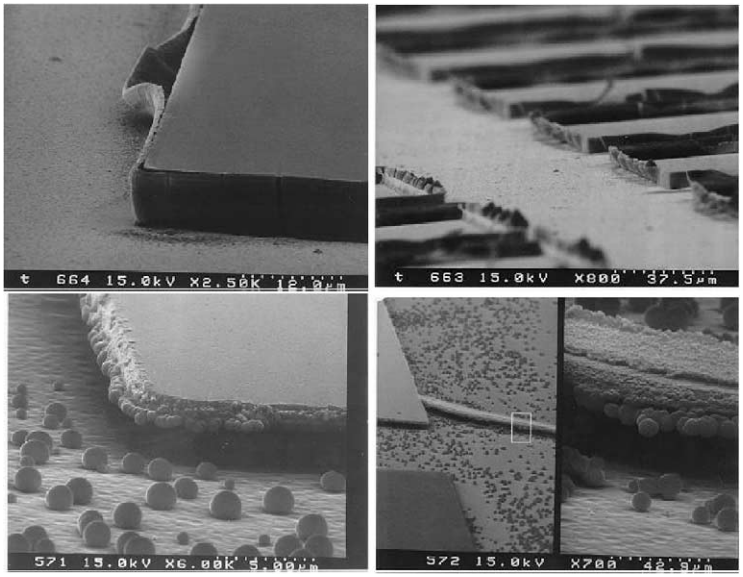

Fig. 1. Various states of gold sputtering with an inert gas: creation of a fence leaning against the photoresist (LHS, top), after removal of the photoresist: the isolated fences (RHS, top), isolated gold spheres and a broken fence… (bottom).

(Fig. 1). Several attempts to etch either gold [4,5] or platinum [6] in chlorine-containing ambients have been reported; but a combined application to actually existing contacts (like the Bell contact or similarly sandwiched metal layers) is still lacking. Hence, in this study we developed a chain of processing steps which are highly selective to each other.

2. Chemical considerations

Titanium. Originally, the Bell contact as developed by Lepselter for contacting contact holes in Si, consisted of four metal layers starting with Pt which reacts with Si to Pt_5Si_2. This has a lot of advantages [1]. Among them are the high electrical conductivity combined with the different color of this compound. In III/V semiconductor processing, the first Pt layer is skipped because Pt does not react to a stable compound. Therefore, it is common to start with a thin layer of Ti ($\leqslant 100$ nm) on top of the semiconductor surface which must be as clean as possible. Ti is easily etched in an chlorine-containing ambient like BCl_3, $SiCl_4$, or Cl_2 itself. The chemical nature of this process is proven by the surface and the sidewalls, which remain perfectly clean without any redeposit. Moreover, the enhancement of the etch rate compared to pure Ar etching is also remarkable.

Platinum. All simple common etchants completely fail to generate volatile compounds. When heated even to medium temperatures ($\geqslant 150^{\circ}C$), they all decompose to the metal and the counter atom according to the reaction

$$PtCl_4 \xrightarrow{\Delta} Pt + 2Cl_2. \quad (1)$$

Therefore, every progress which has been claimed to date has to be attributed mainly to the enhancement of the etch rate of platinum compared to simple sputtering with argon rather than the generation of a Pt compound: it is due to the heavier mass of the incident ion (often Cl_2^+), by which the momentum transfer into the solid is improved [7,8]. This is confirmed by the corresponding communication of redeposits which are proof of the nonvolatility of the claimed platinum compound [6,9–12]. Hence, real chemical strategies have to be applied. These are the following three approaches:

1. Etching with a fluorine source which produces free $F^{\cdot}$ radicals (like CF_4/O_2) to generate volatile, orange vapors of PtF_6.
2. Etching with phosgene, $COCl_2$, or CO/Cl_2 diluted and stabilized with argon to create the volatile carbonyl chloride $Pt[COCl_2]_2$ [13].
3. Etching with PF_3 which generates the volatile compound $Pt(PF_3)_4$ [14].

The first compound, PtF_6, is an orange gas. Its formation is reported at elevated temperatures with elemental fluorine. To avoid this corrosive gas, we chose NF_3 which exhibits the lowest energy of formation known for the conventional fluorine sources [15]. As for the second compound, it is known that is formed even from $PtCl_2$ acting with CO at elevated pressures. Therefore, it should be created under the comparatively

Table 1
Plasma reactors and experimental conditions for CCP-RIE and ECR-RIE

	CCP	ECR
System	PlasmaLab 90	PlasmaLab 90 with AsTeX double magnet system
Pump	Pfeiffer TPH 330	Alcatel 1000 M
Volume (l)	43	43 + 12 (ECR source)
Electrode plate: material	SiO_2	SiO_2, BN, Al
Electrode: diameter (cm)	25	15
Basic pressure (Torr)	3×10^{-7}–1×10^{-6}	$<4 \times 10^{-7}$
Pumping speed (l/s)	215	640
Pressure (mTorr)	20	0.8
Total flow (sccm)	25	40
Reduced pumping speed at working pressure	19	640
Bias voltage (−V)	450–470	25–150
Temperature (°C)	75±3	150±3

very mild conditions of a low-pressure plasma, either with equimolar additions of CO/Cl_2 or with phosgene as reactive component. The third compound is the PF_3 homologue to the compound $Ni(CO)_4$, which is well known to form the only carbonyl spontaneously from an element. As was shown first by Kruck, $Pt(PF_3)_4$ is obtained from $PtCl_4$ by applying PF_3 at elevated pressures of more than 300 bars [16,17]. Compared to these rather hostile conditions, Chatt found out that at atmospheric pressure, the synthesis of volatile *cis*-$Cl_2Pt(PF_3)_2$ was possible (bp : 240°C) [18]. Therefore, this compound is expected to be generated in the highly activated ambient of a high-density, electroncyclotron resonance driven plasma by application of an PF_3 containing ambient on metallic platinum. Due to the high energy of the P–F bond, PF_3 is probably not dissociated, but will attack as an excited molecule or radical.

Gold. The final layer is gold for bonding and long-term stability. Therefore, this is the thickest layer (up to 1/2 μm thick). This requires an extremely reactive process to avoid hare's ears which develop as redeposit at the sidewalls of a thick mask [19]. In principle, gold can be etched in chlorine-containing plasmas consisting of Cl_2 and/or BCl_3, leading to volatile Au_2Cl_6, but many precautions have to be taken since the vapor pressure of $AuCl_3$ (which dimerizes to Au_2Cl_6 as vapor) is very low [20].[3] Moreover, it easily decomposes at elevated temperatures to the monochloride, which has an even lower vapor pressure than the trichloride. Hence, there exists a very narrow working window between sufficiently high volatility (lower temperature threshold) and thermal dissociation (upper temperature limit). The etch rate in BCl_3 is significantly reduced compared with Cl_2 by at least a factor of 3. Since GaAs/AlGaAs is mainly etched with BCl_3 or $SiCl_4$, this behavior is important for further integration into the whole sequence of VCSEL processing. Only in this case, gold can be used as self-adjusting mask for GaAs etching.

[3] $p_s \approx 10^{-6}$ Torr at 60°C and $\approx 10^{-3}$ Torr at 125°C.

3. Experimental: deposition

Polished GaAs wafers were coated by means of e-beam evaporation (Leybold system 560) or RF sputtering (Perkin-Elmer 2400). For gold, the first method is superior to the latter one since the grain size is significantly smaller so that the layer can be denoted as amorphous. Formation of striation-free edges is possible only with these layers. To allow for an exact determination of the etch rate, the thickness of the metal films for the trials reported in this study was around half a micron for Ti and Pt and up to 1 μm for Au. Titanium can be deposited with a very fine grain size using e-beam evaporation as well as using rf sputtering, and comes along nearly amorphous even at a magnification of some $50,000\times$. Due to its high melting temperature, platinum is expected to be deposited with a very fine grain size with both methods. This is actually the case.

4. Experimental: etching

The etching experiments were carried out applying two Oxford Plasma Technology reactors which are extensively described in previous papers [21,22]. The characteristics of both the systems are compiled in Table 1. For the etching, thick photoresist (AZ 4562, *d*: between 6 and 7 μm) has been used applying our trilevel technique as reported elsewhere [21]. Every redeposit

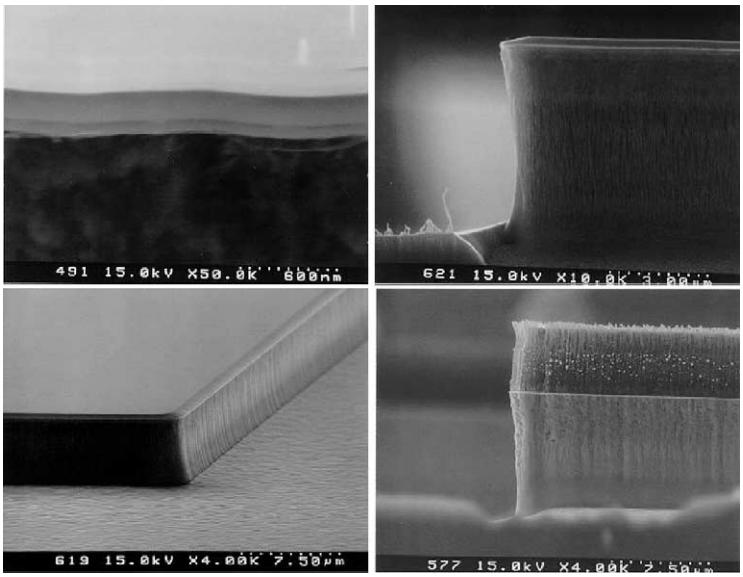

Fig. 2. p-GaAs, topped with Ti/Au (total thickness: 200 nm) and a mask with Al_2O_3 (top) or thick PR (bottom RHS, trilevel technique [22]). The subsequent etching of underlying GaAs in a high-density plasma of Cl_2/Ar is carried out without formation of a sidewall polymer [24] $\Rightarrow$ slight undercut in GaAs, but totally free of any residue at the sidewalls of the photoresist.

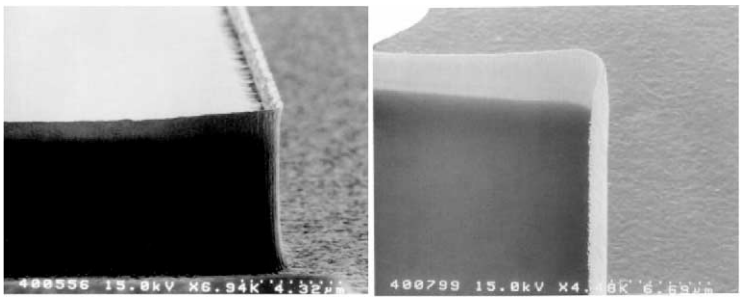

Fig. 3. Etching of platinum with NF_3 does not lead mainly to PtF_6. The remnant fence has been deposited at the flank of the photoresist (LHS) and cannot be removed by ultrasonic cleaning (RHS).

will be visible (which is not quite sure with a "hard" mask of dielectric material like Al_2O_3 or Si_3N_4, cf. Fig. 2). Hence, the absence of any remnants at the edges of the mask is the crucial criterion whether a process is physically or chemically dominated (cf. Fig. 2, bottom RHS).

For Ti and Au, best results at etch rates up to 20 Å/min are obtained in Cl_2 or BCl_3 (even better) with both the kinds of plasmas applied. Etch rates are between 10 and 40 Å/min which is a good process window for thicknesses not thicker than 4000 Å. They are shown with a top layer of alumina in Fig. 2.

The challenge remains the residual-free etching of platinum. With NF_3 and CO/Cl_2, the growth of small fences at the rim of the photoresist cannot be avoided. This means that under the conditions of a high-density plasma, the formation of PtF_6 or the carbonyl chloride $Pt[COCl_2]_2$ is either not exclusively feasible or the formed compounds will decompose at the mask edge (Fig. 3). At least the enhancement ratio of 2 against argon confirms the assumption of PF_6 formation (Fig. 4), which is equivalent to the enhancement ratio of pure PF_3 (also not always free of residues at the mask flanks).

However, it can be seen from Fig. 5 that adding PF_3 to NF_3 will lead to the desired result of etching platinum without any remnants (PF_3 : NF_3 : Ar = 10 : 10 : 2 sccm; $p < 1$ mTorr). However, the enhancement factor compared to Ar, equals a maximum of 4. The etch rates are not high (P_{MW}: 800 W, V_{DC}: -250 V; $T_{surface}$: 205°C): about 20–40 nm/min, but sufficient for a typical

thickness of 100 nm, so it takes 2–5 min to etch through the platinum section of the metal sandwich.

As expected, the etch rate depends on the gas composition. At equal gas flows of NF_3 and PF_3, we observe a broad, but distinct maximum. We attribute this behavior to a two-step procedure: in the first step, bond-breaking between platinum atoms by atomic fluorine, followed by an attack of PF_3 by which the volatile compound is created (Fig. 6).

It should be pointed out that all the etching has to be accomplished before having sintered the metal layers. Due to interdiffusion, a very stable intermetallic compound, Ti_3Pt, will be formed which even withstands the attack of *aqua regia* and which actually acts as diffusion barrier [23,25]. As has been evident, the reactive ion etching of the Bell contact with consecutive etchants

- Au with Cl_2;
- Pt NF_3/PF_3;
- Ti with Cl_2 or BCl_3

is extremely chemical and requires pure metals in a stack of films.

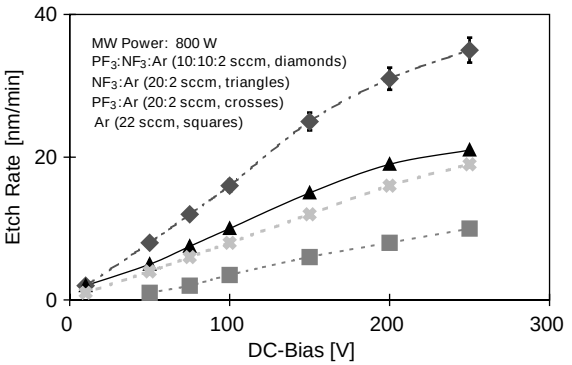

Fig. 4. Pt etch rate as function of gas composition for four gases (three different mixtures and argon, etch rate is parametrized using the most sensitive Pt line at 265.9 nm). It can be seen that the etch rate obtained with argon is enhanced by reactive gases ($2\times$ in NF_3, $>4\times$ in PF_3/NF_3). This is the crucial criterion for a reactive process.

5. Experimental outlook

With this etching sequence, we have shown the feasibility of dry etching of the complete Bell contact.

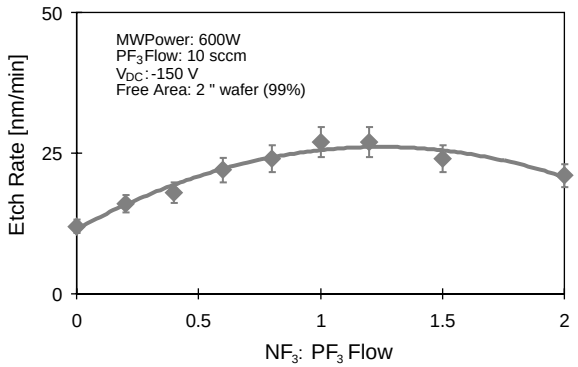

Fig. 6. Pt etch rate as function of gas composition in mixtures of NF_3/PF_3. The maximum at equimolar gas flows is referred rather to chemical than physical reasons.

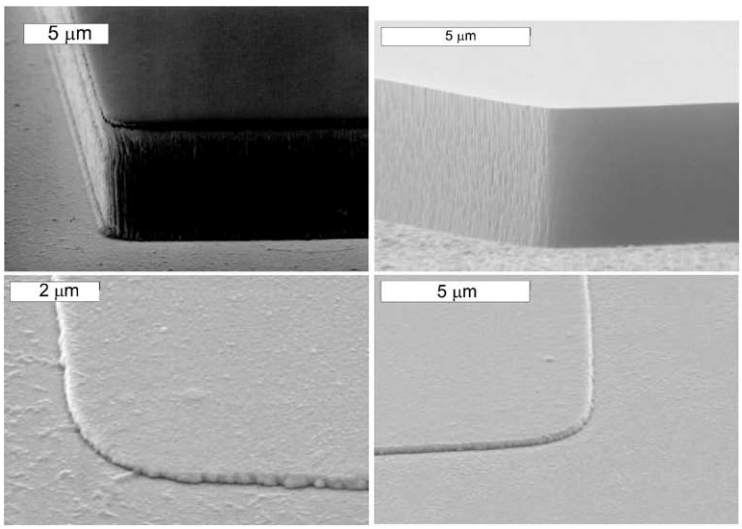

Fig. 5. Comparison of platinum films etched with a PF_3-containing ambient (high-density plasma generated with ECR). The PR mask totally lacks any remnants of sputtered platinum (top and middle). After removal of the photoresist, visual inspection of the surfaces shows that the etching does not roughen the surface significantly (bottom, LHS and RHS).

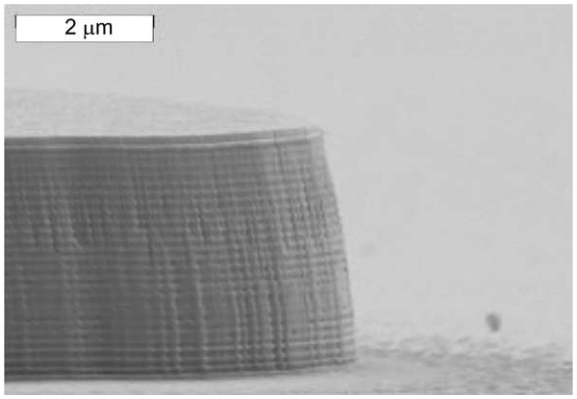

Fig. 7. VCSEL structure as etched with a cap of a platinum (200 nm in thickness) in the high-density plasma of an ECR discharge (BCl_3/Ar).

This has to be integrated into the fabrication process of some optoelectronic devices. We applied the VCSEL structure, protected by a stack of metal layers. As shown in Fig. 7, this stack is highly resistant against BCl_3/Ar which serves as anisotropic etchant for GaAs/AlGaAs. With this process, we can now choose whether we first deposit the metal layers and etch them subsequently, or apply the common lift-off procedure, which is easier to follow, but prone to contamination of the sensitive surfaces which are to be metallized later on.

6. Conclusion

We report on the residual-free etchability of platinum films by application of a high-density plasma containing PF_3/NF_3. Trials with NF_3 as single possible fluorine source or pure Cl_2, $COCl_2$ or CO/Cl_2 failed. Due to the high energy of formation, PF_3 does not dissociate, so it can attack the excited platinum to generate the volatile tetrakis phosphorous trifluoride platinum which is stable enough to pass the dark space sheath of the powered electrode. Therefore, the ambient NF_3/PF_3 is the best suited agent to etch Pt free of residues.

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