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D E C I S I O N
of 22 July 1998

Case Number: T 0453/97 - 3.4.2

Application Number: 88303400.1

Publication Number: 0289174

IPC: G 03F 7/09, G03F 7/26

Language of the proceedings: EN

Title of invention:
Antireflection coatings for use in photolithography

Patentee:
Advanced Micro Devices, Inc.

Opponent:
Philips Electronics N.V.

Headword:
-

Relevant legal provisions:
EPC Art. 56

Keyword:
"Inventive step (yes)"

Decisions cited:
G 0004/93

Catchword:
-



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Case Number: T 0453/97 - 3.4.2

D E C I S I O N
of the Technical Board of Appeal 3.4.2
of 22 July 1998

Appellant: Advanced Micro Devices, Inc.
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Decision under appeal: Interlocutory decision of the Opposition Division
of the European Patent Office posted 27 February
1997 concerning maintenance of European patent
No. 0 289 174 in amended form.

Composition of the Board:

Chairman: E. Turrini
Members: A. G. Klein
B. J. Schachenmann

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Summary of Facts and Submissions

- I. European patent No. 0 289 174 was granted on the basis of European patent application No. 88 303 400.1.

Claims 1 and 2, the only independent claims of the set of claims as granted read as follows:

"1. A method of preparing a wafer surface (12) in an integrated circuit structure for patterning by photolithographic techniques, wherein the wafer surface (12) is a highly reflective aluminum or titanium surface and the surface is coated with an antireflective film (16) before forming a layer (14) of photoresist over the surface, characterised in that the antireflective film (16) consists of titanium nitride, and the titanium nitride is coated to a thickness of between 30 and 50 nm for an aluminum surface and between 15 and 35 nm for a titanium surface, whereby the amount of light reflected from the surface is reduced to less than about 5% of the incident radiation."

"2. A method of patterning a wafer surface in an integrated circuit structure wherein the wafer surface (12) is a highly reflective metal surface and the surface is coated with an antireflective film (16) prior to forming a layer (14) of photoresist over the surface and exposing unmasked portions (22) of the photoresist to optical radiation (18) of a predetermined wavelength, characterised in that the antireflective film (16) consists of titanium nitride, and the metal surface (12) is aluminum or titanium, the titanium nitride being coated to a thickness of between

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30 and 50 nm when the surface is aluminum and between 15 and 35 nm when the surface is titanium, and the wavelength of the optical radiation (18) being related to the thickness of the titanium nitride as follows:

<u>Wavelength</u>	<u>Metal Surface</u>	<u>TiN Thickness Range</u>
365 nm	Al	30-40 nm
405 nm	Al	35-45 nm
436 nm	Al	40-50 nm
365 nm	Ti	15-26 nm
405 nm	Ti	20-30 nm
436 nm	Ti	25-35 nm

II. The patent was maintained in amended form by an interlocutory decision of the Opposition Division.

In the Opposition Division's opinion, the first variant of the subject-matter defined in the granted claims, as directed to the use of aluminium as the wafer surface material, did not involve an inventive step in view of the contents of the documents:

Antireflection coatings on metal layers for photolithographic purposes, H. A. M. van den Berg et al., Journal of Applied Physics, 50(3), March 1979 (hereinafter document D1); and

JP-A-61 185 928 (hereinafter document D2), together with an English translation thereof (D2').

The second variant contained in the granted claims, as directed to the use of titanium as the wafer surface material, was however considered patentable, and the patent was maintained in amended form, with claims restricted to this variant, accordingly.

III. The Appellant (Patentee) filed an appeal against the interlocutory decision of the Opposition Division, requesting that it be set aside and that the patent be maintained as granted.

The Respondent (Opponent), for his part, requested that the appeal be dismissed.

IV. In support of his request the Appellant submitted that the subject-matter of the claims as granted was not rendered obvious by the contents of documents D1 and D2.

He submitted in particular that document D2 did not stress the importance of the thickness of the antireflective film of titanium nitride described therein. The document instead pointed at the strong dependency of the optical reflectance of the antireflective film on the sputtering conditions, which determined its physical structure, and it suggested to further reduce the reflectance of the titanium nitride film by providing an additional organic macromolecular film on top of the aluminium surface so as to flatten its unevennesses.

Document D1 on the other hand theoretically investigated a number of potential antireflective materials on the basis of rather complex equations, and taught that semiconductors such as amorphous silicon and amorphous selenium were most suitable materials for antireflective coatings, thus actually pointing away from metallic titanium nitride. This document indeed indicated that for the materials investigated the optimum value of the quality as expressed by a specific parameter Q was a function of the film thickness, but it was not apparent that the latter parameter was directly equivalent to the optical reflectance. Also, the values given for the optimal thickness of the best

antireflective films were extremely low, leading to very bad results if they were applied to the antireflective films of titanium nitride as disclosed in document D2.

Anyway, in order to arrive at the claimed invention the skilled person starting from the disclosure in document D2 should have proceeded through a series of no less than five distinct steps - including in particular the crucial, non-obvious recognition that the better results reported in Document D1 for amorphous silicon as compared to the values described for this material in document D2 might have resulted from a possible difference in the thicknesses of the respective films.

- V. The Respondent, for his part, maintained that the claimed subject-matter lacked an inventive step.

The alleged invention in particular aimed at providing an antireflective film of minimal reflectance.

Document D2 already disclosed the advantageous optical and technological properties of a titanium nitride film as deposited on an aluminium substrate, which achieved a reflectance of about 10% only and could be etched selectively, i.e. without any loss of the further patterns formed on aluminium and polysilicon, as compared to the properties of a layer of amorphous silicon, which according to document D2 exhibited a reflectance of at least 50% and did not allow for selective etching.

Document D1 on the other hand taught that the antireflective properties of coatings formed on metal layers for photolithographic purposes depended on the thickness of the coatings. The optimal thickness could be easily calculated from the formulae given in the document, as was evidenced by the computed curves filed

with his letter of 9 October 1997. Alternatively, the optimal thickness could be easily determined by way of simple tests, as was also acknowledged in the patent in suit for the titanium nitride films described there. The optimal value of the quality factor Q, which in document D1 was explicitly said to be a function of the thickness, was a combination of the very parameters which, admittedly in a slightly different combination, also defined the reflectance.

VI. Oral proceedings were held on 22 July 1998, at the end of which the Board announced its decision.

Reasons for the Decision

1. The appeal is admissible.
2. *Procedural matters - Reformatio in peius*

Independent claims 1 and 2 as granted each encompass two distinct variants, of which the first involves the preparation or patterning of an aluminium surface and the second the preparation or patterning of a titanium surface.

In the interlocutory decision under appeal the Opposition Division ruled that the first variant lacked an inventive step and it therefore dismissed the Appellant's main request that the opposition be rejected.

The Opposition Division also concluded that the second variant was patentable. Accordingly, it admitted the Appellant's auxiliary request that the patent be maintained in amended form on the basis of a set of claims restricted to said second variant.

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The Respondent did not appeal against the interlocutory decision. Accordingly, following the findings of the Enlarged Board of Appeal in the decisions G 9/92 and G 4/93 (see OJ 1994, 875), neither the Respondent nor the Board may challenge the maintenance of the patent as amended in accordance with the interlocutory decision.

Since challenging the patentability of the second variant of the claims as granted would in effect amount to challenging the maintenance of the patent as amended, the patentability of this variant is an issue which, due to the absence of an appeal by the Respondent, can no longer be questioned in the present proceedings. This was explicitly accepted by the Respondent at the oral proceedings of 22 July 1998.

The present proceedings will therefore be limited, for procedural reasons, to the issue of patentability of the first variant of the subject-matter defined in the granted claims, which involves the preparation or patterning of an aluminium surface.

3. *Novelty of the subject-matter of the first variant of granted claim 1*

3.1 Document D2 undisputedly discloses a method of preparing a wafer surface in an integrated circuit structure, which comprises the features of the preamble of claim 1, in its first variant, and in which additionally the antireflective film consists of titanium nitride, as is further set out at the beginning of the characterizing portion of the claim

(see D2', page 1, claim 1). In this known method the thickness of the titanium nitride film is in the order of 100 nm (see D2', the sentence bridging pages 4 and 5), and the film achieves a reflectance of about 50% (see Figure 3).

The first variant of the method set out in independent claim 1 is thus distinguished from the method of document D2 in that the titanium nitride is coated to a thickness of between 30 and 50 nm, whereby the amount of light reflected from the surface is reduced to less than about 5% of the incident radiation, as indicated at the end of the characterizing portion the claim.

3.2 Document D1 discloses various antireflective films, as deposited in particular on an aluminium surface, of which however none consists of titanium nitride (see Tables I to III on pages 1213 and 1214).

3.3 The remaining prior art documents available on the file do not come closer to the claimed method.

3.4 Accordingly the subject-matter of claim 1 in its first variant is novel in the sense of Article 54 EPC.

4. *Inventive step of the subject-matter of the first variant of claim 1*

4.1 The parties agreed to consider that the nearest prior art is actually constituted by the method of preparing a wafer surface for patterning by photolithographic techniques disclosed in document D2, from which the claimed method is indeed distinguished only in that the titanium nitride film is coated to a thickness of between 30 and 50 nm, instead of a thickness in the order of 100 nm as disclosed in D2 (see point 3.1 above).

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The Appellant's submission that the claimed range allows for reducing the amount of light reflected by the surface during the photolithographic process from about 10% of the incident radiation - as is specified in the third paragraph of page 6 of D2' and shown in Figure 3 of document D2 - to less than about 5% was not contested by the Respondent, and is also in conformity with his calculations effected on the basis of the equations given in document D1 (see the curves of Figure B, C and D filed with Respondent's letter of 9 October 1997).

Document D2 also emphasizes the significance of titanium nitride in terms in particular of its suitability for selective etching, as compared in particular to amorphous silicon (see D2', page 2, 4th and 5th paragraphs). At the oral proceedings the Appellant submitted that the skilled person striving to improve the antireflective film of document D2 should therefore be expected to stick to the titanium nitride material recommended in the document, rather than to seek for a different material.

Accordingly the technical problem underlying the subject-matter of claim 1 as objectively defined in view of this nearest prior art is to still further reduce the optical reflectance of the antireflective film of titanium nitride disclosed in document D2.

4.2 Document D2 does not by itself provide any incentive at investigating the influence of the thickness of the antireflective film on its reflectance, in the expectation of a further substantial reduction.

The document instead expressly stresses the strong dependency of the reflectance of the titanium nitride film on the sputtering conditions, in particular on the electrical bias applied to the baseplate, the quantity

of oxygen in the chamber and the vacuum level (see D2', page 6, third paragraph to page 7, first paragraph). The document also points at the possibility of providing an additional organic macromolecular film between the aluminium layer and the antireflective titanium nitride film to flatten the underlying surface (see the paragraph bridging pages 5 and 6, and Figure 2).

These explicit indications provide clear guidance for the skilled person to seek for possible improvement by further the investigating the influence of the sputtering conditions or the structure of additional layers on the reflectance of the titanium nitride coating, which in effect point away from the claimed solution.

In this context, the Board also notices that the curve of Figure 2 of the patent in suit, which represents the dependency of the reflectance of the titanium nitride film on its thickness, and the very similar curves submitted by the Respondent all exhibit the following remarkable characteristics:

- the reflectance of titanium nitride films is relatively constant around the thickness of 100 nm disclosed in document D2;
- this reflectance at first slightly increases when departing from the known value of 100 nm towards lower thickness values;
- the desired decrease of the reflectance below 5% is only achieved in a narrow range of thickness values - which, for a given wavelength as used in photolithographic processes, is still narrower

than the claimed range of between 30 nm and 50 nm applied to the g-, h-, and i-lines of the mercury spectrum as a whole (see page 4, lines 4 to 16 of the description of the patent in suit);

- this narrow range is centred on a thickness which is relatively far away from the known value of 100 nm (less than half that value); and
- for still smaller thicknesses the reflectance again increases to values much above the value of about 10% at the known thickness.

As a consequence of these remarkable characteristics of the dependency of the reflectance of a titanium nitride film on the film thickness, the skilled person could not, in the Board's view, be expected to discover the claimed range in an obvious way in the course of routine experiments he would perform when putting into practice the teaching of document D2.

- 4.3 However, it is still to be examined whether the remaining prior art would have incited the skilled person to envisage any closer investigation regarding the influence of the thickness of the antireflective film on its reflectance, in a reasonable expectation of an improvement of the antireflective film of document D2.

- 4.3.1 The only further document relied upon by the Respondent in the opposition and appeal procedure is document D1.

Document D1 is a scientific article specifically dedicated to antireflection coatings as used for alleviating the problems caused by the reflection by

metal layers of the radiation used for photolithographic purposes (see the Title), in which "a number of materials are theoretically investigated and experimentally tested" (see the Abstract).

In the introductory part of the document the blurring of images formed in high conducting substrates is attributed to the existence of standing waves in the resist layer. A solution consisting in introducing a spacer satisfying a couple of equations (1) is given for a substrate consisting of **dielectric** material (see page 1212, Introduction).

In a theoretical portion it is stated that absorbing substrates like metals were much more complicated. Accordingly, for this case the standing-wave ratio of the amplitude of the plane waves in the resist - which in substance corresponds to the square root of the optical reflectance of the spacer - is expressed in complex equation (2). The equation involves the real and the imaginary parts of the refractive indices of the resist, spacer and substrate, the thickness of the spacer and the wavelength of the radiation and includes exponential expressions. A further complex equation (3) involving the same parameters, also with an exponential term, has to be fulfilled for both the real and the imaginary part if no standing wave shall exist in the resist. The article then goes on to state that "there are three degrees of freedom in this equation: both values of the complex refractive index of the spacer and the thickness h_2 of this layer. Consequently, from a theoretical standpoint a complete set of materials can be selected which satisfies Eq. (3)", to end with a number of recommendations as to the choice of an adequate material: "If we intend to cover Ni with a dielectric layer, a material is required with a refractive index equal to 9.9. All actually existing

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dielectric layers possess a refractive index which is much lower"; "But most materials like metals and semiconductors proved to be inappropriate ...", and "The thickness over which the amplitude of the wave reflected at the metal-spacer boundary is matched to that of the reflected wave is too small compared to the phase shift that can be achieved over this distance. The suitable materials can be distinguished by a high ratio n/k . The proper elements are to be found in the semiconductor group and especially in those semiconductors with a large band gap" (see pages 1212 and 1213, Theory).

The next chapter of the article is dedicated to the results. It starts with the statement that "The following elements appear to be suitable to serve as the spacer: amorphous silicon, amorphous selenium, and the well-known Cr_2O_3 ". Follows the definition, in an equation (4), of a value Q mentioned to be a good standard for the quality of the system which, however, does not exactly correspond to the definition of the reflectance. The optimal value of Q , which should be as low as possible, is explicitly said to be a function of the thickness of the spacer h_2 . Tables I to III respectively summarize the behaviour of a number of combinations of spacers and metal layers, for three wavelengths of the spectrum of mercury sources. The tables contain the optimal values for the standing-wave ratio, the quality factor Q and the thickness of the spacer, as calculated on the basis of equations (2) to (4) and of the complex refractive index data available from the various bibliographical sources also indicated in the tables (see page 1213, Results).

Finally, the chapter Discussion at the end of the article concludes with the statement that "Tables I-III demonstrate very clearly that a great improvement can

be expected by using spacers. The semiconductors Si and Se, in particular, show a remarkable reduction of the quality factor Q . Cr_2O_3 is considered somewhat less helpful, the data available for As_2Se_3 being, however, very promising. Concerning the experimental aspect, the article essentially states that - since a relatively large scatter was found in the data presented about semiconductors depending upon the method in which the layers were prepared - spacers made of Si, Se and Cr_2O_3 were deposited on several substrates. The reproducibility of the processes used was very good, the scatter in the optical properties completely satisfactory and a reduction of the exposure time by a factor of more than 10 could be obtained, with an enormous increase of the range over which the exposure time could be varied (see pages 1213 and 1214, Discussion).

4.3.2 Thus, in the Board's view, from an objective assessment of the actual contents of document D1 it emerges that:

- the document is an essentially theoretical article on the antireflective properties of coatings formed on metal layers, based on complex mathematical equations used to calculate various parameters from data as available from various bibliographic sources;
- the article is clearly dedicated to the selection of appropriate antireflective film materials;
- the article strongly advocates the use of semiconductor materials for such antireflective film materials;
- the article explicitly points at the fact that the relevant equations cannot always be satisfied, for any material; and

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- the article confirms the statement made also in document D2 that the optical properties of the antireflective films are strongly dependent on the deposition conditions.

On the other hand the statement in the appealed decision that document D1 "discloses a method for calculating the optimum thickness of an antireflective film on a metallic surface" (see page 7, point 20) does not appear to correctly and objectively summarize the actual content of the document.

Concerning the thickness of the antireflective films, document D1 indeed mentions that - **for the materials recommended there** - there is an optimal theoretical value of the thickness, for which a certain parameter Q , standing for the film quality, is optimal. The tables also disclose calculated optimal thickness values, most of which are much lower than the claimed range and, if applied to the titanium nitride film of document D2, would lead to an increase of its reflectance rather than to the desired reduction.

- 4.3.3 The document does not however address the sensitivity of the reflectance of the films to variations in their thickness, and it does not in particular clearly disclose the remarkable shape of the curve representing the variation of the reflectance of a film as a function of its thickness, with its pronounced narrow minimum, as apparent from Figures 2 and 3 of the patent in suit.

This particular shape, and consequently the effect of selecting the film thickness within the narrow range corresponding to the minimum, are indeed evident from the curves filed by the Respondent which, he submitted, were obtained from equation (2) of document D1.

However, in the absence of any other hint at investigating in more details the effect of the thickness of a film on its reflectance, the skilled person, in the Board's view, had no obvious reason to draft these particular curves, using the film thickness as an only variable in equation (2), if not by hindsight. Given the strong dependency of the optical properties of antireflective films upon the deposition conditions, which is stressed both in documents D1 and D2, the skilled person would not have expected any substantial improvement from an optimization of the film thickness. He had no reason to suspect that the optimum thickness referred to in document D1 actually corresponded to a marked minimum of the reflectance, i.e. to a reduction in the reflectance value mainly due to the thickness and not negligible in comparison with the expected influence of the variations in the film deposition conditions. Given the complexity of the equations disclosed in D1, the occurrence of such minimum, in the Board's view, could not have been predicted from a mere, unbiased reading of document D1 by the skilled person.

4.3.4 The Board cannot either endorse the Respondent's argument that the skilled person would have recognized that the difference between the value of the reflectance of a film of amorphous Si as referred to in document D2 (about 50% as shown on Figure 3) and the value which he might have calculated from the tables in document D1 (about 2%) necessarily resulted from a difference in the thickness of the layers, and that, accordingly, the value given in document D2 for the titanium nitride film could be improved as well by properly selecting its thickness.

However, in view of the consistent statements made in documents D1 and D2 as to the strong dependency of the optical properties of the films upon the deposition

conditions and in the absence, for the above reasons, of any clear hint in the prior art at any comparably relevant impact of the thickness of the films on their reflection properties, the skilled person would have ascribed the discrepancy referred to above to possible differences in the deposition conditions of the films.

Even if one admitted that the skilled person, in view of the theoretical values given in document D1 for an amorphous Si film, could actually have suspected that the bad reflectance values reported in document D2 for amorphous silicon resulted from an inadequate selection of the thickness of the Si film, he still had no obvious reason to suspect that the same was true for the much better antireflective film of titanium nitride film described there in detail.

4.3.5 The documents cited in the European Search Report and not relied upon by the Respondent do not come closer to the claimed subject-matter.

4.4 For the above reasons, the available prior art does not, in the Board's view, provide any clear encouragement for the skilled person to proceed to any closer investigation of the influence of the thickness of the titanium nitride film known from document D2 on its light reflexion properties, which only could have led him to discover the occurrence of a marked minimum and its significance in respect of the desired reduction of the film's reflectance.

The method of the first variant of claim 1 is therefore considered to involve an inventive step in the sense of Article 56 EPC.

5. Independent claim 2 is directed to a method of patterning a wafer surface, which in substance comprises all the steps of the preparation method of claim 1, with further limitations consisting in additional steps of forming a layer of photoresist and of exposing it, and in a narrower definition of the thickness ranges as a function of the wavelength of the exposing radiation.

The subject-matter of this independent claim and, obviously, also the subject-matter of dependent claim 3 as appended to claim 2, therefore also involves an inventive step in the sense of Article 56 EPC.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The patent is maintained as granted.

The Registrar:

E. Görgmaier



The Chairman:

E. Turrini

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