UDC 621.382.049

MECHANICAL STRESSES IN THIN METAL FILMS USED IN SCHOTTKY DIODES

V. Solodukha[1], Dr. Sc. V. Baranov[2], Ph.D. J. Solovyev[1],
Dr. Sc. A. Tourtsevich[1], Ph.D. S. Dick[2], Ph.D. I. Tsyrelchuk[2]

[1]JSC "Integral", [2]Belarusian State University of Informatics and Radioelectronics,
Belarus, Minsk
baranov@ieee.org

Research results on the mechanical stresses in thin metal films based on refractory metals for Shottky diodes and VLSIs applications are presented. A new diagnostics method for mechanical stresses in thin films is based on the analysis of the profiles of test structures that are formed by etching the investigated thin films on the silicon substrates.The maximum content of defects in Mo films is observed at the substrate / film interface.

Keywords: metal films, mechanical stresses, method.

Thin films are widely applied in devices of solid-state electronics (Shottky diodes) and VLSIs applications. Thin films based on using non-organic dielectrics on the surface of crystal substrates of silicon, GaAs and other semiconductors are produced by thermal oxidation (SiO_2 on silicon substrates) or by methods based on vapor-transport reactions (Si_3N_4, SiO_2, Al_2O_3). Thin metal films (Al, Cu, Ti, Mo, W, Ni, Pt, Pd and other metals and alloys) as a rule are deposited by vacuum methods. Still in both cases the films thickness rests much less than the dimensions of the substrate.

During manufacture of devices on the basis of the film-substrate solid-state structures they have many times subjected to thermal treatments. The temperatures rise up to 550°C and higher. Due to the differences in temperature liner expansion index (TLEI) of the substrate materials and films the mechanical stresses develop in the solid state structures and in some cases it may have a result in substantial substrate deformation process similar to that of a bimetal wafer case. This is not desirable due to additional errors in reproduction of layout pattern during lithography stages. On the other hand, due to relative closeness of modules of resilience of materials of substrates and films and due to difference in their thicknesses about of an order of magnitude, mechanical stresses are mostly effective in the films material.

The purpose of the current study is to find out how the mechanical stresses are distributed per thickness of the films made of metals with different physical properties. Integral mechanical stresses in thin films made of, for instance, Mo were studied previously in [1, 2].

EXPERIMENTAL METHODS

During the experiments, wafers of monocrystal silicon (100) of the thickness of 380±20 μm were used. Thin films of Al — 1%Si alloys (up to 0.6 μm thickness) as well as those of Mo, Ni and their alloys with Re and V accordingly (~0.15 μm thickness) were coated by magnetron sputtering of high purity targets. The number of uncontrolled impurities in them was less than 0.07%. E. g., targets made of refractory metals were produced by vacuum smelting. While before applying Al films the surface of silicon wafers was oxidized, Mo and Ni films were coated immediately to the silicon surface, and before loading into a vacuum chamber the wafers were treated in liquid solution.

During the sputtering stage Al of not less than 99.99% was used. While coating Al films, the temperatures of silicon substrates varied from the room temperature to 350°C, and those for Mo and Ni films were approximately 280°C. During magnetron sputtering process other conditions also varied: pressure; power supplied to the magnetron source; operation current of silicon wafers heater which established their temperature during film coating; and target voltage. These factors in principle affect Ar ion absorption by the film, nature of its formation and the rate of growth on substrate, as well as the value of residual mechanical stresses in the film. Film coating rate, e. g. of Al, was approximately 0.15 μm/min. After finishing thin film coating the wafers were treated in vacuum for their natural cooling. The rate of cooling was not more than 10°C/min.

Film thickness control was done using optical interferometer and SEM in particular Hitachi-806. The films were also studied in Perkin Elmer PHI-660 (USA) and Auger-electron spectrograph. To find the integrated value of residual mechanical stresses (σ) a double-crystal layout spectrometer and an X-ray diffractometer were used. Calculations were made as per $\sin^2\varphi$ method [3]. While studying films of Al alloy, a thin layer of Si (40 nm of thickness) was also coated in the same vacuum cycle.

The part of samples with Mo and Ni films was subjected to chemical etching through a P/R mask to determine the etching bias, which can be quantitatively estimated by the width of the inclined part of Δ profile or by φ angle. Methodical difficulties when estimating etching angle appear if the slope angle of side wall of the film element is over 90°. In this connection we propose a new method based on making the so called "chops" of solid state structures which were then analysed using SEM where they were observed as profiles.

Also determined were the parameters of film morphology, in particular, the grain size. Here Hitachi H-800 electron microscope was used for transmission and reflection of electron diffraction pattern.

Experimental results and discussion

It has been found that in Al — 1%Si films, near the boundary of their separation from the substrate (mostly within the film), there is a transition layer that we have called the relaxation layer. Chemical bonds between the film and substrate materials are strong enough to form a solid-state structure. Similar items were discussed in [4].

The relaxation layer is also present in the films of the studied refractory metals (Mo and Ni) and in the films of their alloys it was less tangible.

Pure Mo films were deposited by magnetron sputtering at a certain pressure of argon in order to achieve their optimum mechanical properties. Then measurements were taken of residual stresses and etching bias value depending on the given factors which, taking all together, may change the nature of crystallite nucleation and growth.

One of the cross-sections of the substrate/film solid-state structure is shown on Fig. 1. Thus, a certain etching angle is visible at the border of the substrate and the film (φ_Σ), actually in silicide formation zone.

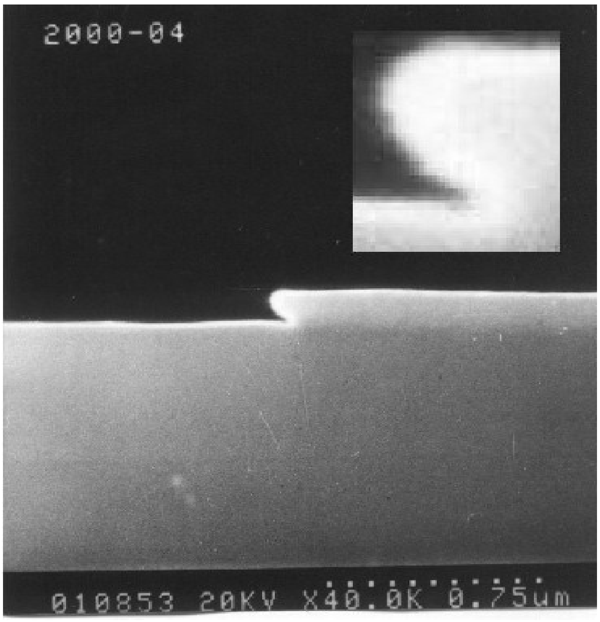

Fig. 1. A cross-section of the structure: substrate / refractory metal thin film

Increase in power of a sputtering magnetron source results in some decrease of σ. This fact is related to formation of Mo film, which has a certain structure in plane (100).

Isothermal annealing of a solid state Si/Mo structures, that follows next, sets up preconditions for developing the process of re-crystallization of those parts of the structure which experience major stresses. Besides, due to the reciprocal diffusion in the transition layer of Si/Mo contact there forms one or several phases of Mo silicides which have isomorphic structure with the initial metal film. At the same time, due to greater specific volume of the new phase and differences in physical properties of the silicide layer regarding Mo the integral value of σ in the film changes. It is very difficult to preliminarily account for contributions of all the components (conditioned by changes of the transition layer properties — resilience modules, re-crystallization temperature, TLEI, etc.). Thus, in this work we relied on the experimental data, in particular, on the obtained thin film profiles.

Analysis of these profiles reveals that distribution of the value of residual mechanical stresses as per thickness substantially differs for the films obtained at different conditions of their forming.

In fact, if one assume that the film structure is uniform as per all its cross-section, and if one takes into account that the process of chemical etching has the isotropic character, then the hypothetical profile of the film after etching will have the appearance that can be characterized as “positive etching bias”. This kind of film profile is dissolving those parts of metal film, which are not protected by a P/R mask. Any ununiformities of the film structure (impurities, crystal composition defects, residual stresses before and after relaxation, etc.) result in changes in film etching rate which is recorded when observing the profile.

Since it is established that the studied Mo films have uniform chemical composition in thickness, it is quite reasonable to suppose that higher film etching rate in certain cross-section planes or in nano-size thickness layers is conditioned either by high defects density or by substantial residual stresses. However, as a result of conducting re-crystallization annealing, the most probable cause is excessive presence of defects in the said nano-size layers. Thus, for samples with most substantial residual stresses in the initial film, the etching profile differs from the expected one for isotropic process of uniform film etching, and even “negative etching bias” may be formed. Nano-size film layers, which immediately contact substrate, etch at lower rate due to formation the silicide transition layer. This result proves the validity of our conclusion on existence of the relaxation layer in films, which is located close to the surface of separation with substrate, also for metal films with low Mo ductility.

Fig. 2 shows the case when the transition layer has lower local mechanical stresses at the border substrate/metal film.

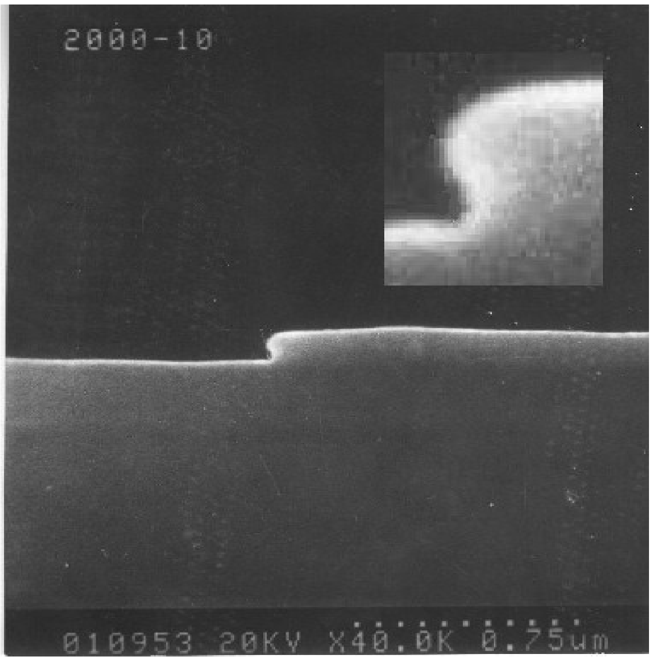

Fig. 2. A cross-section of the substrate/refractory metal thin film with lower mechanical stresses at the border taken using SEM

If we compare the obtained profiles one can estimate defect distribution as per supposed “nano-size layers” of thin film. We consider that it is difficult to solve this task using other known methods.

One can also assume that the ideal etching profile corresponds to absence of residual mechanical stresses in a thin film.

Table 1 consists of some experimental data on the calculated residual stresses in thin Mo films correlated with the etching angle (φ_Σ).

Table 1

Etching angles depending on mechanical stersses in Mo films

Etching angle (φ_Σ), °	77	87	98	124
Residual stresses (σ_Σ), GPa	–0.2	+1.0	+1.9	+2.7

As one can see from the table, σ_Σ changes from compressing (–) to tensile (+) units when changing the etching angle from values less than 90° to 124°.

The data corresponds to [5] where, however, the bulk properties of material are delivered.

In Al — 1%Si alloy thin films located on mono-Si substrates, due to different TLEI of contacting materials, there forms a transition layer with increased presence of defects, which are located near the substrate/film interface. This layer effectively accumulates injection impurities (Si), and in the layer there occurs relaxation of residual mechanical stresses. Thus, we called this layer a relaxation layer.

By film profiles formed after local etching one can definitely find distribution of the residual mechanical stress value alone film profile. This can be regarded as a new method of research of thin film properties, and here the integral value of stresses in film correlates to the etching angle and to the value of "etching bias".

Changes in conditions of Mo film forming (P_{Ar} and power of discharge of magnetron source of sputtering) substantially affect the film texture and residual mechanical stress value. Maximum presence of defects in Mo films, due to deformation brought about by residual mechanical stresses, is observed in a thin layer adjoining the border of substrate/film interface.

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В. А. Солодуха, В. В. Баранов, Я. А. Соловьев, А. С. Турцевич, С. К. Дик, И. Н. Цырельчук

Механические напряжения в тонких металлических пленках, используемых в диодах Шоттки.

Представлены результаты исследований механических напряжений в тонких пленках на основе тугоплавких металлов применительно к технологии диодов Шоттки и СБИС на основе кремния. Новый метод оценки механических напряжений основан на анализе профилей структур, формируемых локальным травлением пленок на пластинах кремния. Максимальная дефектность пленок Mo наблюдается на границе раздела «пленка — пластина».

Ключевые слова: *металлические пленки, механические напряжения, метод.*