Measurement and Control of a Residual Oxide Layer on $TiSi_2$ Films Employed in Ohmic Contact Structures

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***Abstract*—An inadvertent oxide layer is formed on a titanium disilicide ($TiSi_2$) film following various wet and dry processes in a manufacturing environment. The use of H_2SO_4:H_2O_2:H_2O (1:1:5) as a wet etch for excess Ti metal, prior to the high temperature anneal used to form a subsequent $TiSi_2$ layer, is identified as the source of the undesired oxide via multi-wavelength spectroscopic ellipsometry and Auger electron spectrometry studies. This inadvertent oxide layer on $TiSi_2$ is shown to form bad electrical contacts and is a contributing source to large standby currents in polysilicon gate shunts. Spectroscopic ellipsometry is shown herein as a unique analytical tool to determine both the thickness and structure of this poorly structured oxide during process development. A single wavelength ellipsometer monitoring scheme for both the appearance as well as the thickness of this inadvertent oxide layer is proposed for use in high-volume manufacturing.**

I. Introduction

Titanium disilicide ($TiSi_2$) with its low resistivity and refractory nature has been employed for the gate, contact, and interconnect metallization of CMOS devices [1], [2]. The formation and electronic properties of $TiSi_2$ films have been well-studied [3]–[5]. Less-studied, to our knowledge, is the very thin oxide layer formed on $TiSi_2$ that occurs in a manufacturing environment due to the use of various wet cleans in tandem with high-temperature anneals. This oxide layer has been used by some process engineers as a convenient etch stop in later contact etch processing. However, unless the oxide thickness is well controlled, its use poses risks to yield and reliability as we show herein. S. Murarka *et al.* [3] and others have studied the oxidation of $TiSi_2$, and found that the silicide oxidized to form a SiO_2 surface layer similar to oxide growth on poly-Si, where oxidation occurs by a mechanism in which silicon diffuses through the silicide and oxidizes at the silicide-SiO_2 interface. However, they did not study wet etch (H_2SO_4:H_2O_2:H_2O) initiated oxide growth which occurs during a high-temperature anneal in nitrogen, as we describe below.

In order to provide better control, process and metrology engineers need to know both the structure and thickness of the thin oxide on top of the silicide film. Single wavelength optical ellipsometry, as employed as in an IC manufacturing plant, measures the optical parameters of the unknown oxide film, t, n and k, where t is the film thickness, n is the unitless index of refraction, and k the extinction coefficient [6]. This method works well only if the underlying films' optical properties are well-characterized beforehand. Hence, a simple method to monitor thin SiO_2 on top of $TiSi_2$ in manufacturing is not readily apparent, because the optical parameters of both the unknown top oxide layer and the contiguous underlying silicide layer must be known beforehand in order to accurately determine the bi-layer film properties using traditional single wavelength ellipsometry. Underlying silicide optical properties are often unavailable and, moreover, the oxide grown on $TiSi_2$ is not a perfectly structured silicon dioxide and optical constant values must be assumed.

Spectroscopic ellipsometry (SE), as employed in research environments, uses a variety of wavelengths to determine $t, n,$ and k of unknown multi-layer film systems [7]–[10], as well as to determine the void structure and, in some cases, the film composition through data regression. In this paper, we employ the SE technique to unambiguously determine both the oxide layer thickness on top of underlying $TiSi_2$ and the SiO_2 void structure for two types of oxide growth conditions on $TiSi_2$, which we term inadvertent and intentional oxides for reasons that will become apparent below.

First is the silicon oxide layer inadvertently formed during the high-temperature thin film annealing process used to form $TiSi_2$. The oxidation is initiated by washing the Ti coated wafer in an oxidizing agent such as H_2SO_4:H_2O_2:H_2O $(1:1:5)$ during cleaning of excessive metal titanium and prior to the high-temperature anneal in a nitrogen ambient that forms $TiSi_2$ intentionally and the oxide inadvertently. Later, we show that by choice of a different wet etch chemistry, if desired, this inadvertent oxide layer formation can be eliminated entirely. The second group of oxide layers consists of $TiSi_2$ films intentionally annealed in an oxygen ambient for different times to grow various thickness oxides of known optical properties [3] to be used for comparison purposes with the first group of inadvertent oxides.

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The remainder of the paper is divided into the following sections: Section II summarizes both the desired and inadvertent oxide formation conditions; Section III provides the measured properties for both the inadvertent and the intentionally grown oxides on $TiSi_2$; Section IV illustrates two detrimental effects to electronic circuits arising from the inadvertent oxide; and Section V gives the conclusions and suggestions for improved process control.

II. Intentional and Inadvertent Oxide Growth Conditions

A. Inadvertent Oxide Growth

The $TiSi_2$ films are grown on a (100) p-type silicon substrate via a two-step process. After ion-sputtering titanium thin films on the silicon substrate, rapid thermal annealing at 850°C is used to form silicide layers several thousand angstroms in thickness. A thin oxide layer may also be grown inadvertantly on top of the $TiSi_2$ film due prior wet cleaning with sulfuric acid, H_2SO_4, and hydrogen peroxide, H_2O_2, which removes excessive metal titanium on undesired areas but also acts as a hidden oxygen source for subsequent parasitic oxidation. The thin parasitic oxide layer on $TiSi_2$ was analyzed by Auger electron spectrometric analysis (AES) to determine the film's thickness. We employed the known sputter rate of thermally grown SiO_2 as a calibration standard, even though the oxide layer on $TiSi_2$ has many more void sites in its structure than perfect SiO_2. This film depth scale ambiguity is incorporated in the horizontal axis of Figs. 1(b) and 2(b). Finally, we note that the inadvertent oxide layer may be entirely eliminated by using the RCA wet etch solution, $NH_4OH:H_2O_2:H_2O$ (1 : 1 : 5) [11], for the removal of excessive titanium instead of the $H_2SO_4:H_2O_2:H_2O$ solution. Oxide-free $TiSi_2$ films are made using the RCA wet etch solution for the studies of Section II-B. described below.

B. Intentionally Grown Oxide

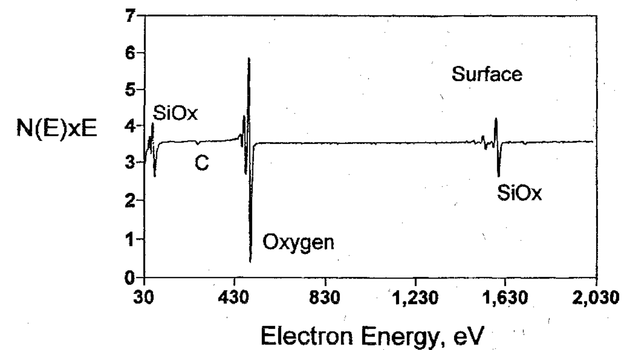
A control group of thin SiO_2 films on underlying $TiSi_2$ is intentionally fabricated by a high temperature (1050°C) thermal anneal of $TiSi_2$ in an oxygen ambient for varied periods of time to create different oxide thicknesses on underlying $TiSi_2$ films. In these studies, we observed composition changes in the Ti-Si layer versus the various anneal times as more fully described below. Nevertheless, we still use these films as a standard because of their similarity to the $TiSi_2$ films of Section II-A.

III. Inadvertent Oxide Layer Properties

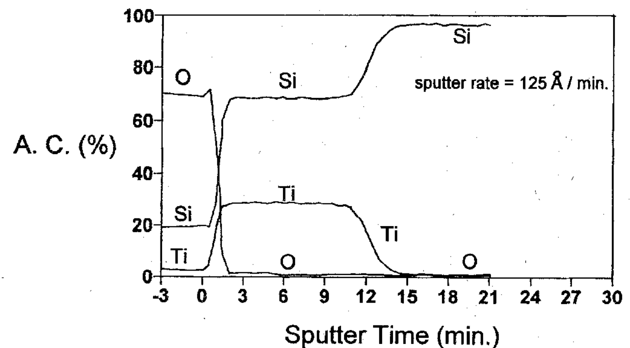
Below, we provide partial analysis of the bi-layer film properties of the thinly oxidized silicide in Sections III-A (AES data) and III-B (ellipsometer data.)

A. Auger Electron Spectrometric Analysis

AES data for the undesired parasitic oxide (growth procedure II-A) on the $TiSi_2$/Si contact structure is shown in Fig. 1. The silicide has uniform $TiSi_2$ stoichiometry as desired, and a clearly distinguishable oxide layer at the surface which consists of silicon oxide with a trace amount of carbon contamination. The estimated oxide thickness is 163 Å. Fig. 2(b) illustrates the AES profile of the oxide-free reference $TiSi_2$ film, prepared using the RCA $NH_4OH:H_2O_2:H_2O$ solution instead of the $H_2SO_4:H_2O_2:H_2O$ solution employed in the results of Fig. 1. The top oxide layer thickness in Fig. 2 is impossible to determine by AES because the thickness of this layer is much less than the minimum strip step of the ion-mill (a few atomic layers) of standard SiO_2. We used these oxide free samples to study the optical parameters of the underlying $TiSi_2$ layer on silicon in further ellipsometry measurements as described below.



(a)



(b)

Fig. 1. Auger electron spectrometry data of a $TiSi_2$ film with an inadvertently grown silicon oxide surface layer 163 Å thick due to the use of a wet $H_2SO_4:H_2O_2:H_2O$ strip. (a) Survey spectrum on sample surface shows silicon oxide layer on top of film; (b) depth profile displays the varying film stoichiometry versus sputter time. The thin surface oxide layer is indicated by the oxygen peak at $0 < t < 0.5$ min.

B. Spectroscopic Ellipsometry Analysis

Spectroscopic ellipsometry, with its multiple probe wavelengths, has distinct advantages over single wavelength ellipsometry. In single wavelength ellipsometry, one measures Δ and Ψ, which are complex functions of film thickness, and index of refraction (real n and imaginary k). The complex amplitude refraction ratio is given by $\rho = \rho_p/\rho_s = \tan(\Psi)\exp(\Delta)$ where ρ_p and ρ_s are the refraction coefficients in the parallel and perpendicular directions. In the case of a

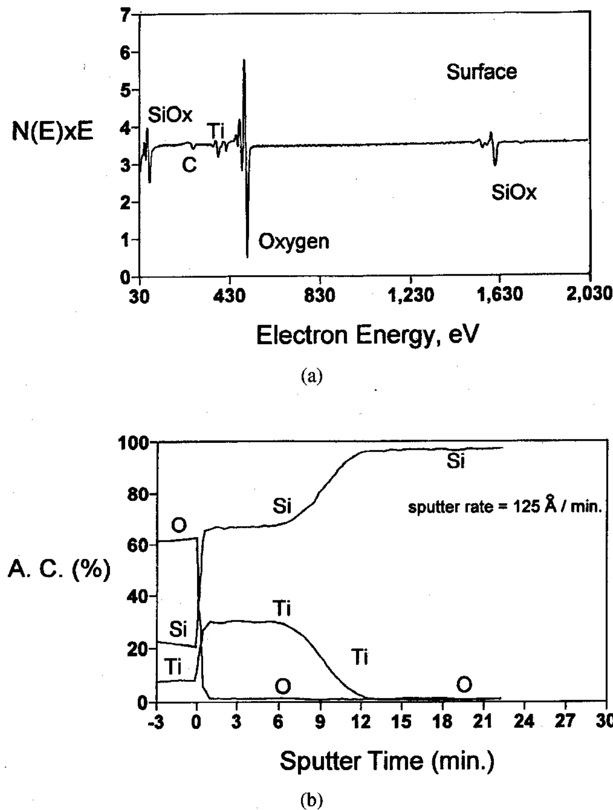


Fig. 2. (a) Auger surface survey spectrum and (b) Auger depth profile of clean $TiSi_2$ film with negligible surface oxide growth by means of a wet $NH_4OH:H_2O_2:H_2O$ strip replacing the $H_2SO_4:H_2O_2:H_2O$ of Fig. 1. Comparison with Fig. 1(b) shows no oxygen peak at $0 < t < 0.5$ min, indicating an oxide-free surface.

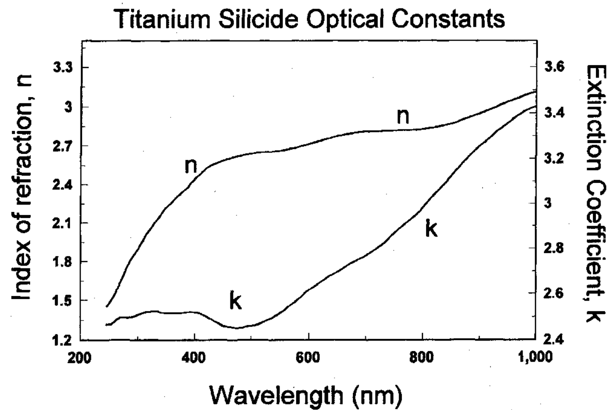


Fig. 3. The optical constants of the oxide free $TiSi_2$ film measured over the range from 200 to 1000 nm as described in text and as shown in Fig. 2. n is the unitless index of refraction and k is the extinction coefficient. The data was provided by J. A. Woollam Co., Lincoln, Nebraska.

single layer film such as SiO_2 on top of a known substrate such as Si, we usually assume the imaginary part of refractive index is known, which relates to the absorbance of the film. Given Δ and Ψ, one can then easily determine film thickness and index of refraction. In the case of multiple-layer thin films, or a single-layer film composed of two known materials such as voids and SiO_2, single-wavelength ellipsometry can't determine three variables. For example, film thickness, index of refraction, and composition in each layer cannot all be found. Spectroscopic elliposometry on the other hand can determine Δ and Ψ over an entire wavelength range, thereby allowing one to minimize the difference between experimental and thoeretical curves via data regression. This provides much more external freedom to determine, for example, the three properties of each layer, such as film composition, thickness and index of refraction. In spectroscopic ellipsometry, the index of refraction of mixed films, such as SiO_2 with voids, are treated using the mean field approximation. A model based on multiple-layer films can be constructed, and the total calculated optical response is compared to the experimental optical response. Parameters such as layer thickness, index of refraction, and composition are adjusted so that the variance of the calculated model and real data is minimized. Under these conditions, we judge the model is a good representation of the multi-film system.

Spectroscopic ellipsometry, in our case, uses the wavelength range from 200 to 1000 nm to study the inadvertently oxidized films, the intentionally oxidized films, and the oxide-free $TiSi_2$ films. By determining the amplitude and polarity changes at each wavelength, the optical properties of a multi-layer film can be determined. The operational practice involves recording the optical response (Δ and Ψ) for the entire spectrum range, constructing a stacked film model, and minimizing the error between the model and the experimental data from the measured values by the least square fitting procedure. We first employed SE on the oxide-free $TiSi_2$ film to experimentally obtain the optical parameters of the underlying $TiSi_2$ film. The $TiSi_2$ optical constants as measured versus wavelength in this spectral region are shown in Fig. 3. Next, we measured the inadvertently oxidized $TiSi_2$ films as given in Section II-A from 200 to 1000 nm and calculated the optical parameters. For this calculation, we used the previously measured n and k from the oxide free $TiSi_2$ sample as the proper optical constants for the underlying $TiSi_2$. Curve fitting also was used to match the measured optical data with the parameters of a film structure model. The optical parameters, n and k, of the inadvertent silicon oxide layer 163 Å thick with 36% void fraction on the $TiSi_2$ film best fitted the measured data.

The spectroscopic ellipsometry study of the intentionally grown oxide layers on $TiSi_2$ shows that the oxide layer growth and Ti-Si layer composition both are changing during the thermal anneal cycle in an oxygen ambient as summarized in Fig. 4. The higher temperature process makes silicon migrate into the $TiSi_2$ structure to form a silicon rich Ti-Si layer. The longer the oxidation time, the thicker the oxide layer grows, causing more silicon to migrate into the Ti-Si layer, as shown in Fig. 4.

Although SE is a powerful tool for diagnosis of thin films, it may not be suitable for a manufacturing or production line environment due to both the complexity of data fitting and the cost of ownership. In manufacturing conditions where the optical parameters are repeatable even if the exact nature of the film stoichiometry or void fraction is uncertain, the limited task of monitoring oxide layer thickness grown on

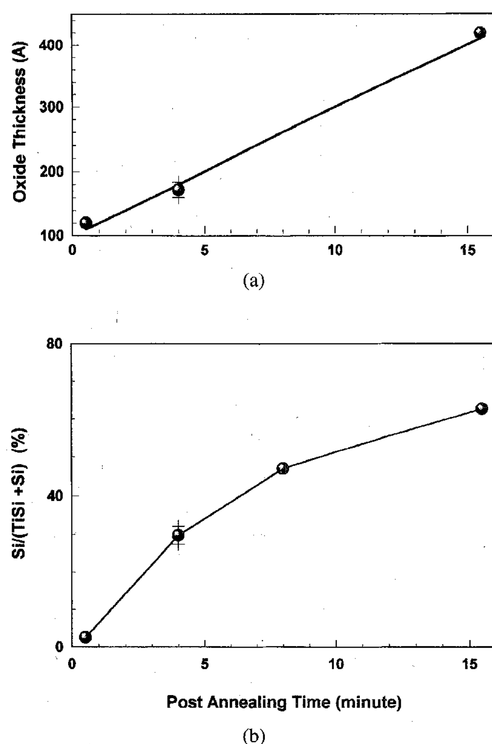


Fig. 4. Results of post annealing in an oxygen ambient at 1050°C for various times. (a) The dependence of the intentional silicon oxide layer thickness on post anneal time. (b) The silicon percentage in the Ti-Si film for various post anneal times.

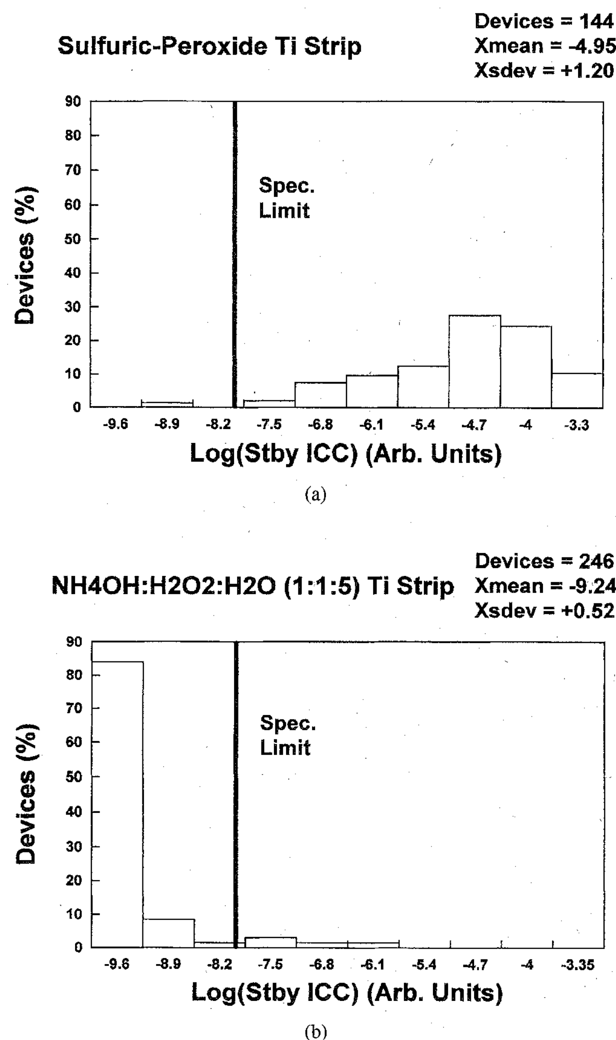


Fig. 5. (a) The histogram of standby current of test SRAM circuits using the H_2SO_4:H_2O_2:H_2O Ti wet strip of reference 11. (b) The histogram of standby current for the NH_4OH:H_2O_2:H_2O wet strip test runs. The spec. limits, shown by thick vertical lines, indicate the maximum allowable standy ICC.

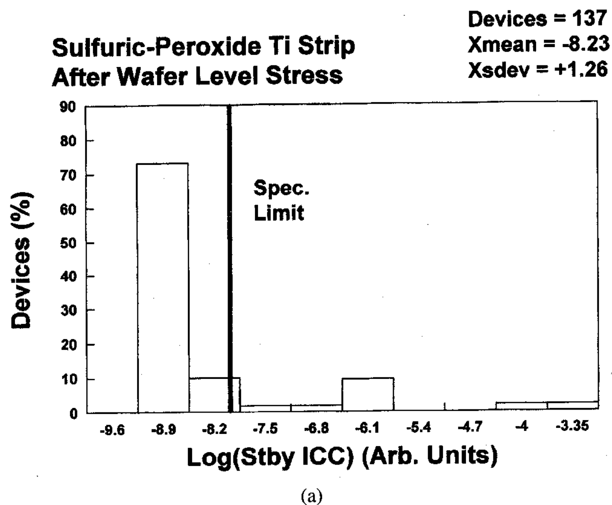
$TiSi_2$ may be simplified. The optical constants of $TiSi_2$ film are pre-measured by the SE technique and assumed unchanged from run to run. Then one or two wafers per cassette can be monitored with conventional single-wavelength ellipsometry. However, to do this reliably the underlying $TiSi_2$ optical constants must be measured every few weeks using spectroscopic ellipsometry to avoid errors in oxide thickness monitoring caused by changes in the $TiSi_2$ film properties.

IV. Detrimental Effects of Inadvertent Oxide on Yield and Reliability

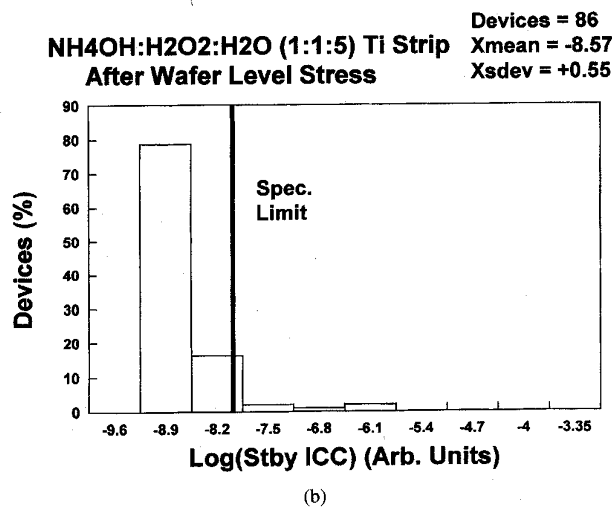
For process engineers who employ the inadvertent oxide as a subsequent etch stop in later contact etches a word or two of caution seems appropriate. In addition to the danger of increasing the contact resistance beyond acceptable limits, the wet sulfuric Ti strip process also appears to reduce yield and reliability by causing undesired leakage paths across the poly spacer. Fig. 5(a) and (b) shows two CMOS standby current populations for a specific test circuit (SRAM) split between two wet cleans. Fig. 5(a) is for the H_2SO_4:H_2O_2:H_2O wet strip prior to anneal and Fig. 5(b) is for the NH_4OH:H_2O_2:H_2O wet strip prior to anneal. Due to proprietary industrial data issues the absolute current values in Figs. 5 and 6 are absent but the trends are still clear. The group processed using H_2SO_4:H_2O_2:H_2O shows a markedly higher average standby current above the manufacturing standby current specification limit set for this circuit as indicated by the thick vertical line.

A similar CMOS test circuit in a different manufacturing process did not show any significant difference in standby current distribution between wafers processed using H_2SO_4:H_2O_2:H_2O and using the NH_4OH:H_2O_2:H_2O wet strip. However, a major difference was observed subsequently after wafer level stressing at elevated temperatures and supply voltages. Fig. 6(a) and (b) shows the two standby current distributions observed after stressing. Clearly, the change in the standby current distribution between the two wet strips is a reliability concern. It may also reduce the maximum operational frequency of some electrical circuits. In addition, the first CMOS test circuit described above also showed similar behavior after wafer level stress. Functional failures due to this mechanism have not been observed even in parts with high standby current.

Subsequent failure analysis of the effected parts typically revealed leakage between the gate and the source/drain on single transistors that employed the H_2SO_4:H_2O_2:H_2O wet



(a)



(b)

Fig. 6. (a) The histogram of standby current measured after wafer level stress for H_2SO_4:H_2O_2:H_2O Ti wet strip test runs. (b) The standby current measured after wafer level stress on circuits using the NH_4OH:H_2O_2:H_2O solution of [11] for wet Ti strip test runs.

strip. In most cases there was not convincing evidence to distinguish gate oxide defects from silicon defects. The lack of visible defects coupled with the change in failure rate between the two wet strip chemistries leads to the conclusion that the H_2SO_4:H_2O_2:H_2O leaves leakage paths on the poly spacer. A proposed mechanism is a "$TiSi_2$" stringer across the polysilicon spacer. This could be explained by oxide formation properties of the H_2SO_4:H_2O_2:H_2O. A thin layer of "$TiSi_2$" is judged to be formed on the spacer oxide during the first anneal. The H_2SO_4:H_2O_2:H_2O strips the Ti metal but forms an oxide on the thin "$TiSi_2$" layer over the spacer. This self-passivates the layer and no additional metal strip takes place. The unstripped layer forms a high resistance path between the gate and source/drain across the poly spacer. The ability of this material to act as an antifuse during wafer level stress is not currently understood. No failure of parts occurred with the H_2SO_4:H_2O_2:H_2O wet strip which does not passivate the $TiSi_2$ layer and continues to etch into the $TiSi_2$.

V. CONCLUSIONS

The inadvertent oxide layer formed on top of $TiSi_2$ films via wet cleaning followed by subsequent furnace anneals has been studied using spectroscopic ellipsometry and Auger analysis. The inadvertent oxide thickness and its control are crucial if the oxide layer is to be used later as an etch stop without encountering contact resistance problems or standby current leakage issues. This study indicates that the complete elimination of the inadvertent oxide layer may be required for yield and reliability reasons. A simple method for production monitoring of this layer's appearance as well as its thickness is suggested based on a single wavelength ellipsometry measurement of each production lot, coupled by periodically applying spectroscopic ellipsometry.

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