Molybdenum silicide in infrared emitting devices

Baldauf, Julia, Schmidt-Grund, Rüdiger, Reiche, Manfred, Ortlepp, Thomas
Molybdenum silicide in infrared emitting devices

Julia Baldauf*a, Rüdiger Schmidt-Grundb, Manfred Reichea, Thomas Ortleppa

a CiS Forschungsinstitut für Mikrosensorik GmbH, Konrad-Zuse-Straße 14, 99099 Erfurt, Germany; b Technische Universität Ilmenau, Institut für Physik, 98684 Ilmenau, Germany

ABSTRACT

We present and discuss the infrared properties of molybdenum silicide thin films, molybdenum silicide photonic crystals and the electromigration of molybdenum silicide.

Magnetronsputtered and annealed molybdenum silicide layers were investigated via infrared spectral ellipsometry.

Simulations of optical properties of molybdenum silicide photonic crystals [metal-insulator-metal structures] show that properties influenced by the size of the structures differ to those of widely used photonic crystals made of Ag. The infrared absorption of MIM-structures comprising of a solid molybdenum silicide layer and one molybdenum silicide layer in form of disks were simulated for different disk diameters and layer thicknesses. A first maximum of absorption (at about 2740 nm) is almost independent of the diameter of the molybdenum silicide disk. A second maximum of absorption (7120 nm -7750 nm) shows an increase of its resonance wavelength with increasing disk diameter. A third maximum of absorption (at about 11000nm) instead shows a respective decrease. In the simulations the thicknesses of the metal layers and the dielectric layer were varied. Changes in the thickness of the dielectric layer caused greater changes in the absorption spectra than changes in the thicknesses of the metal layers. For the application in thermal emitters, the knowledge of electromigration properties of molybdenum silicide layers is crucial. Investigations via accelerated tests with different acceleration factors are demonstrated for test structures. We investigated structures based on molybdenum silicide and for comparison with a well known system analogous structures made of aluminium. We find that molybdenum silicide shows considerably lower electromigration than aluminium.

Keywords: infrared, infrared emitter, molybdenum silicide, optical properties, photonic crystal, electromigration

1. INTRODUCTION

To tune the optical properties of an infrared light-emitting or light-absorbing device a photonic crystal can be used. Photonic crystals can be realized via periodically structuring bulk materials or via creation of a stack of layers as for example in form of a pile of metal layer, dielectric layer, and metal layer. To engineer the optical properties, one of these metal layers can be periodically structured and layer thicknesses can be altered. For the metal layers often gold1 or silver2 is used. Unfortunately, gold and silver are not CMOS-compatible. To enable the integration of the production of photonic crystal structures in CMOS-compatible processes demands the use of other materials. Further, thermal infrared emitting devices operate at several hundred degrees Celsius. Thus, for allowing as high as possible operation temperatures, a material with a high melting point in combination with a photonic crystal structure might favor a huge additional gain in optical output power in the desired wavelength range.

Because of its high temperature stability, its high melting point3 and CMOS-compatibility molybdenum silicide is an interesting material for the fabrication of infrared emitting devices and thus for CMOS compatible micro heaters in micro electromechanical systems (MEMS)4,5.

*jbaldauf@cismst.de; phone +49 361 663 1432; www.cismst.de


Proc. of SPIE Vol. 11293 112930Y-1

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 05 Mar 2020
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use
For the use of molybdenum silicide in infrared emitting devices that work via resistive heating, its electromigration properties need to be considered. During current flow, the force influencing the ion, oftentimes called electron wind, can be described as:

$$\vec{F} = Z \cdot e \vec{E}$$  \hspace{1cm} (1)

wherein $Z \cdot e$ is the effective charge, also considering the direction of the exchange of the ions momentum\(^7\). A mathematical model typically used for the description of electromigration\(^7\) is the so-called Black’s equation

$$t_{50} = \frac{A \cdot j^6}{50 \cdot \exp \left( \frac{E_A}{kT} \right)}.$$  \hspace{1cm} (2)

Therein $t_{50}$ is the time to failure for 50% of the conducting lines, $j$ is the current density with the exponent $n$, $E_A$ is the activation energy, $A$ is a constant depending on the geometry of the conducting structure, $k$ is the Boltzmann constant, and $T$ is the temperature.

Values for $n$ and $E_A$ have to be determined experimentally. For the determination of the activation energy $t_{50}$ is measured at different temperatures applying the same current density. For determining $n$, measurements of $t_{50}$ have to be made at constant temperatures while varying the current density. For $1 < n < 2$ the failure is a result of a combination of the formation of voids and further growth of already existing voids. For $n > 3$ the failure is considered to result from Joule heating of the conductor and a temperature gradient\(^6\). $E_A$ is dependent on the mechanism of migration, e.g. the migration through the metal lattice, the migration along grain boundaries, the migration along boundaries and surfaces. Black’s equation is used to extrapolate the time of failure of the devices dependent on the conditions of use and to get an estimation of the reliability of the structures. To gain knowledge about electromigration mostly the time to failure is measured. To this end, the structures are heated externally and operated at a current density higher than the standard operation case, the resistance is measured regularly and the time to failure of every structure is evaluated.

Electromigration properties of molybdenum silicide thin films are rarely investigated in the literature. Some findings show the electromigration of aluminum from the contacts through Molybdenum silicide thin films\(^8\),\(^9\),\(^10\). Bamboo-like layers of molybdenum silicide with a thickness of 250 nm deposited on a double insulator film of Si3N4/SiO2 were investigated at room temperature with current densities between $10^5$ and $10^7$ A/cm\(^2\) until a catastrophic degradation was experienced\(^8\). Investigations of molybdenum silicide heating elements with a thickness of 0.92 µm and NiSi-Ag films as electrical contacts showed a formation of oxides on the surface and a change in the electric resistance when used in oxygen containing atmosphere\(^11\). After a longer time of operation cracks have been found in the molybdenum silicide layer\(^11\). For molybdenum silicide heaters using platinum as electrical contact, a decrease of the heating area takes place which could be traced back to a formation of platinum silicide (PtSi) close to the electrodes\(^5\). All of the above-mentioned effects are considered for an accurate evaluation of its electromigration properties.

2. SAMPLE PREPARATION AND OPTICAL MEASUREMENTS

For the optical investigation 150 nm and 60 nm thick molybdenum silicide layers were deposited on a $<100>$ silicon substrates via magnetron sputtering onto a cold substrate ($1^\circ$C) under a pressure of $5 \times 10^{-3}$ mbar in an Ar atmosphere. The optical properties of these layers were investigated via infrared spectral ellipsometry after annealing of the layers in a N\(_2\) atmosphere at a temperature of 1000 °C. The electromigration properties were investigated using test structures deposited on a $<100>$ double side polished silicon wafer. On this wafer a 200 nm thick layer of silicon oxide was grown. On top of this a 50 nm thick silicon nitride layer was deposited via low pressure chemical vapour deposition and subsequently annealed in nitrogen atmosphere at a temperature of 1050°C for 30 minutes. Afterwards a 175 nm thick molybdenum silicide layer was magnetron sputtered without substrate heating (black part in Figure 1) and the structure was annealed at 1000°C in nitrogen atmosphere. A 900 nm thick aluminum silicide layer (blue part in Figure 1) was deposited as electrical contact. Finally, the entire structure was annealed in hydrogen atmosphere for 30 minutes at a temperature of 350°C. The test structures are line structures with a length of 400 µm and a width of 25 µm or 50 µm.
The refractive index and absorption coefficient (Figure 2) of the molybdenum silicide layers were determined by standard transfer matrix analysis of infrared ellipsometry spectra, using a Kramers-Kronig consistent b-spline model dielectric function approach.

3. OPTICAL SIMULATIONS

The optical properties of the molybdenum silicide based and Ag based photonic crystal structures were simulated with VirtualLab of LightTrans International UG (www.lighttrans.com) Build 7.0.035. The geometry of the simulated structures were metal-insulator-metal structures with metal disks as the top layer, because of disks being the most widely investigated structures \(^2\) (see Figure 3). As bottom layer, a cohesive molybdenum silicide layer with a homogenous layer thickness (hereafter called thickness \(3\)) and optical constants as shown above are used. For the dielectrics used as second layer, the optical constants of silicon dioxide were taken from Ref. 12. The topmost, structured metal layer consists of circular molybdenum silicide disks of a specific diameter and thickness, arranged in a square grating with a pitch of 2 \(\mu\)m. To compare the behavior of the simulated spectra of molybdenum silicide photonic crystals to the typically used photonic crystal structures, spectra of analogous structures but using Ag as metal were simulated. The optical parameters of Ag were taken from Ref. 13.
Figure 3. Schematic of the simulated structures.

4. RESULTS

For the Ag photonic crystal structures (thickness 1=100 nm, thickness 2=20 nm, and thickness 3=100 nm) with different disk diameters, the simulated absorption, which is related to its emission properties is shown in Figure 4.

Figure 4. Absorption of Ag photonic crystals in dependence on the disk diameter.
Figure 5. Absorption of molybdenum silicide photonic crystals in dependence on the disk diameter.

The absorption maxima vary depending on the disk diameter. With an increase of the diameter from 800 nm to 1.3 µm the maximum shifts from a wavelength of 4260 nm to 6190 nm. The absorption at these maxima is between 49% and 50%. Another absorption maximum is located in the spectral range around 9920 nm for disks with a diameter of 800 nm yielding an absorption of 4.7%. This maximum shows an increase of the absorption and its central wavelength with an increase in the diameter of the Ag disks reaching a wavelength of 10590 nm and an absorption of 28.1% for disks with a diameter of 1.3 µm.

For molybdenum silicide structures a dependency of the spectral position and absorption value on the disk diameter is found for two of the three observed absorption maxima. The third maximum in the range of 2740 nm seems to be almost independent of the diameter of the disks. This absorption structure shows a shoulder with a small local maximum at 4260 nm for the smallest diameter, increasing with the disk diameter to a wavelength of 5100 nm. The following maximum of the absorption has a value of 27% and shifts from 7120 nm to 7750 nm with increasing disk diameter. The full width at half maximum of this absorption-maximum decreases for increasing disk diameters. The height of the absorption maximum at about 11000 nm decreases for increasing disk diameters from a value of 16.73% to 11.79%. Additionally this maximum shows a shift in its center wavelength to higher wavelengths. The absorption of the maximum in the range of 2740 nm could result from a resonance between the two metal layers which would explain its independence of the disk diameter.

To investigate the influence of the thicknesses of the layers on the absorption spectrum, changes of the thicknesses in the range of ±5 nm of the metal layer 1, the dielectric layer 2, and the metal layer 3 have been considered. For this investigation, the metal disk diameters were set to 1 µm, while each, thickness1=100 nm, thickness2=20 nm, and thickness3=100 nm of the layers was varied. The difference of the absorption spectra ΔAbsorption = A(λ)\text{i} - A(λ)\text{k}, where \text{i} stands for thickness1 … 3, \text{j} = 100nm, 20nm and 100 nm, and \text{k} = \text{j} ± 5nm for the photonic crystal structures made of Ag are shown in Figure 6. The changes in the spectra induced by varying the dielectric layer thickness (maximum of Δabsorption for changes of the thickness of the dielectric layer =44.7) are at least one order of magnitude greater than the changes induced by varying the thickness of the metal layers (maximum of Δabsorption for changes of the thickness of the metal layer=2.8).
Figure 6. Absorption-difference spectra for variation of the layer thickness for the Ag photonic crystals.
Figure 7 shows similar findings for the absorption spectra of photonic crystal structures made of molybdenum silicide. Here, the influences of the variation of the layer thicknesses are smaller than the changes induced in the spectrum of Ag photonic crystals for all the layer variations.

The simulated absorption spectra of molybdenum silicide photonic crystal structures show the possibility to tune the absorption or emission properties of infrared emitting devices in the spectral range 5 µm to 9 µm and in the range of 10.5 µm to 12 µm by varying the disk diameter. Variations of the disk diameter of Ag photonic crystal structures yield much greater changes of the center wavelength of the first maximum (range 2µm to 7µm) than for similar structures made of molybdenum silicide. No significant changes in the absorption depending on the disk diameter were found for Ag photonic structures in the wavelength range of 11 µm to 13 µm.

The impact of variations of the layer thickness of the dielectric layer on the absorption spectra is greater than variations of the metal thicknesses for both, Ag and molybdenum silicide. Therefore, for the fabrication of the discussed photonic crystals the layer thickness must be set highly accurate.

5. ELECTROMIGRATION OF MOLYBDENUM SILICIDE

The preparation of test structures for electromigration and their measurements were performed according to actual JEDEC standards. Measurements were carried out for up to 2000 h in environmental atmosphere at $T = 130^\circ$C using direct current with current densities of 6.84E+3 A/cm² and 3.42E+3 A/cm² for the structures having widths of 25 µm and 50 µm, respectively. In addition, analogous test structures with Al layers (Al, 1%Si) were also measured in order to compare the electromigration behaviour of molybdenum silicide thin layers with the well-known behaviour of aluminium.

The specific resistivity of the molybdenum silicide thin films was determined to 1.9340±0.0999 Ω mm²/m at 130°C in the initial condition of the layer. The changes of the resistance of the 25 µm and 50 µm test structures was below 0.17% and 0.22%, respectively (see Figure 8).
Analyses of the accumulated failure rate for aluminum and molybdenum silicide samples at 130°C are shown in Figure 9 for test times up to 2000 hours. A significant increase of the time to failure (TTF) exists for molybdenum silicide in comparison to Al. The $t_{50}$ value (equation (2)) is $3.94 \times 10^5$ hours for molybdenum silicide samples and therefore more than a factor of two higher than for similar Al samples ($t_{50} = 1.57 \times 10^5$ hours). Furthermore, it is remarkable that the slope of both curves in Figure 9 appear to be equivalent. There is only a shift between both curves, which might refer to similar sources of errors for electromigration in both materials. Activation energies $E_A$ between 0.3 and 0.5 eV were extracted for Al samples indicating that grain boundary diffusion is a dominant process.

The current exponent $n$ in equation (2) was determined by measurements of 25 µm wide test structures at environmental conditions and at a temperature of 130°C. The current density was varied between $6.86 \times 10^3$ A/cm² and $2.29 \times 10^5$ A/cm² for these experiments. The negative exponent $n$ is then calculated from the slope of the curve of the mean time to failure (MTF) vs. the current density $J$ in a double logarithmic plot. This is shown in Figure 9 resulting in a value of $n = 0.41$ for molybdenum silicide layers, which is slightly higher than for similar Al layers tested at the same temperature ($n \approx 0.3$). Both values of the current exponent refer to a strong effect of stress migration in the electromigration of molybdenum silicide and aluminium at $T = 130°C$. 

![Figure 8](image-url)  
Figure 8. Relative changes in resistance of molybdenum silicide test structures during test in atmosphere at 130°C.

![Figure 9](image-url)  
Figure 9. Plot of the accumulated failure rate vs. the time to failure (TTF) for Al and molybdenum silicide test samples (Left). A double logarithmic plot of the mean time to failure (MTF) vs the current density $J$ for molybdenum silicide test samples (Right). All measurements at $T = 130°C$ for 2000 hours.
6. CONCLUSION

We investigated the electromigration properties and infrared optical properties of molybdenum silicide thin films and simulated the absorption of molybdenum silicide photonic crystal structures in the infrared spectral range. The molybdenum silicide photonic crystals absorption spectra in the infrared showed one maximum of the absorption of up to 54.4% which showed nearly no dependency on the disk diameter, although the absorption spectrum in general depends on the disk diameter. Variation of the thicknesses of the Ag and molybdenum silicide layers also influence the absorption spectra, but much less than the thickness variation of the dielectric layer. For the absorption maxima which were strongly dependent on the disk diameter, similar changes of the absorption spectrum with a variation of the layer thickness have been observed. Molybdenum silicide photonic crystals are an option if the desired wavelength of the absorbing or emitting device is supposed to be in the wavelength range 5 µm to 9 µm. For smaller wavelengths 3 µm to 5µm, no significant changes in the spectra can be achieved with varying the structure properties. Here, other materials such as silver can be used. We have shown that for the fabrication of the discussed photonic crystals the layer thickness must be set highly accurate, with the dielectric layer thickness being the most crucial parameter. Concerning the electromigration, the $t_{95}$ value of 3.94E5 hours found here for molybdenum silicide promises a high life time of micro heaters comprising this material.

Our studies indicate molybdenum silicide having a high lifetime in thermal infrared emitting devices and its possible use in photonic crystal structures to tune the infrared emission of these devices in the spectral range of 5µm to 9µm.

REFERENCES


ACKNOWLEDGEMENTS

Parts of the research were funded by the german „Bundesministerium für Wirtschaft und Energie“ (BMWi) in the program “FuE-Förderung gemeinnütziger externer Industrieinrichtungen in Ostdeutschland- Innovationskompetenz Ost” (VF160030).