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The growth and diffusion barrier properties of atomic layer deposited NbN_x thin films

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Abstract

NbN_x thin films were grown by the atomic layer deposition method using niobium chloride and ammonia as precursors. The deposition temperature was varied between 250 and 500 °C. The film properties were analyzed by energy dispersive X-ray spectroscopy, time-of-flight elastic recoil detection analysis, X-ray diffraction, and the standard four-point probe method. Additionally the diffusion barrier properties of approximately 10 nm thick NbN_x thin films deposited at 350, 400, and 500 °C were studied. As a comparison the barrier properties of Nb(Ta)N and Nb(Ti)N thin films deposited at 400 °C were studied. The breakdown temperatures of the annealed Cu/barrier/Si structures were determined from the X-ray diffraction data, sheet resistance values, and etch-pit results.

Keywords: ALD; Diffusion barrier; Niobium nitride

1. Introduction

Niobium nitride thin films have many potential applications. The superconducting and mechanical properties of NbN have been investigated most extensively. The superconductivity of NbN was invented already in 1941 by Justi et al. [1] and the highest T_c measured for NbN is approximately 17.3 K [2]. NbN has been studied as a possible material for low temperature superconducting electronics, for example in superconducting tunnel junctions [3–6]. The high melting point [7], thermal stability [8], chemical inertness [9], and good mechanical properties [10–12] such as hardness and toughness make NbN a useful material as a hard coating in extreme conditions. Multilayered thin films, for example TiN/NbN and Si_3N_4/NbN, have also been studied as protective coatings [8,13,14]. NbN thin films have also been studied as possible cathode materials in vacuum microelectronic devices [15–17]. On the other hand transition metal nitrides such as TiN, TaN, and WN have been extensively studied as barrier materials to prevent the copper diffusion into silicon. Diffusion barriers could be a potential application for NbN thin films also because the material possesses properties desired from a good diffusion barrier. In addition, NbN is thermodynamically stable towards Cu because of the absence of the Cu–Nb compounds [18].

The barrier material has to fulfill very strict demands; it may not react with the under- or overlaying materials during the manufacture and the operation of the device, it has to have good adhesion to the adjacent materials, low resistivity, and low impurity contents. Good conformality is required in the modern high aspect ratio microelectronic devices as the barrier thickness is predicted to decrease to only 7 nm in the 65 nm node by the year 2007 [19]. Physical vapor deposition (PVD) methods, especially sputtering, have mainly been used to deposit NbN thin films [3,4,6,9,10,14]. However the conformality of the films deposited by PVD methods is only modest which limits their use in fabrication of microelectronic devices. Better conformality can be obtained with the chemical vapor

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deposition (CVD) methods but only a few papers concerning the CVD of NbN thin films have been published. Oya and Onodera [20–22] deposited superconducting NbN thin films at temperatures above 900 °C using $NbCl_5$, NH_3 and H_2 as precursors. NbN thin films have been deposited at lower temperatures (200–400 °C) when niobium dialkylamido compounds tetrakis(diethylamido)niobium [$Nb(NEt_2)_4$] and pentakis(dimethylamido)-niobium [$Nb(NMe_2)_5$] and ammonia were used as precursors [23]. The deposited films were amorphous with a composition of Nb_3N_4, and the resistivity varied between 1000 and 10 000 μΩ cm. Later nuclear magnetic resonance studies showed that $Nb(NEt_2)_4$ actually consists of a mixture of three compounds [24]. When this mixture was heated the composition changed entirely to ethylimidotris(diethylamido)niobium(V) [EtN=$Nb(NEt_2)_3$].

One of the most promising techniques to enable the deposition of conformal thin films is atomic layer deposition (ALD) [25–27]. In ALD the gaseous precursors are alternately introduced to the substrates and between the reactant pulses the reactor is purged with an inert gas. When the experimental conditions are properly chosen the film growth proceeds via self-limiting saturative surface reactions with no detrimental gas phase reactions. As a result, the film thickness is easy to control and the deposited films have excellent conformality and large area uniformity. The good quality and the perfect conformality of the films deposited by ALD make it a promising technique to be used for a variety of microelectronic applications.

The ALD technique has already earlier been used in the deposition of NbN films [28–31]. The ALD of NbN films has mostly been studied at temperature as high as 500 °C [28,30,31]. The films were deposited using $NbCl_5$ and NH_3 as precursors with or without an intermediate Zn pulse that served as an additional reducing agent. According to the composition analyses performed by time-of-flight elastic recoil detection analysis (TOF-ERDA) and Rutherford backscattering spectrometry (RBS) the films were almost chlorine free [28,30] and the resistivities were about 200 and 550 μΩ cm for films deposited with and without Zn, respectively [30]. The ALD deposition of NbN films at lower temperatures (300 and 400 °C) has been only briefly mentioned by Juppo et al. [29]. The NbN films deposited from $NbCl_5$ and NH_3 contained considerable amounts of chlorine, 24 at.% at 300 °C and 15 at.% at 400 °C, and the resistivities of the films were high (>10 000 μΩ cm at 400 °C). In the same study NbN films were also deposited using 1,1-dimethylhydrazine (DMHy) as a nitrogen source instead of ammonia. The film deposited from $NbCl_5$ and DMHy at 400 °C contained 5 at.% of chlorine and had a resistivity of 2900 μΩ cm.

In this work NbN_x thin films were deposited by the ALD method from $NbCl_5$ and NH_3. In contrast to the earlier studies with high deposition temperatures, in the present work low deposition temperatures down to 250 °C were also explored. The barrier properties of NbN_x thin films deposited at 350, 400 and 500 °C were studied and compared with those of Nb(Ta)N and Nb(Ti)N thin films deposited at 400 °C.

2. Experimental details

The films were deposited using a flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Helsinki, Finland) operated under a pressure of about 10 mbar. Nitrogen gas (99.9995%), generated by Nitrox UHPN 3000 nitrogen generator, was used both as a carrier and purging gas. The precursors used were $NbCl_5$ (99%, Aldrich), $TiCl_4$ (≥99.0%, Fluka), $TaCl_5$ (≥99.8%, Merck), and NH_3 (AGA Gas Ab, 99.998%). $NbCl_5$ and $TaCl_5$ were evaporated from open boats held inside the reactor at a temperature of 90 °C. $TiCl_4$ was kept in an external container at a constant temperature of 21 °C and was pulsed into the reactor with the aid of a solenoid valve. Ammonia was led into the reactor through a mass flow meter, a needle valve, and a solenoid valve, and the flow rate was adjusted to 14 sccm (standard cubic centimeter per minute) during a continuous flow. The films were deposited on 5×5 cm^2 silicon and borosilicate glass substrates. The films deposited on glass substrates were used only in the crystallinity studies. In order to deposit NbN_x thin films $NbCl_5$ and NH_3 were pulsed separately into the reactor. The pulse times used for $NbCl_5$ and NH_3 were 0.1 and 1.0 s, respectively, as those were reported to give the highest deposition rate [28]. The length of the purge pulse was 0.5 s. The ammonia dose used in this study was higher than in previous studies. Elers et al. [28] used 8 sccm as the flow rate of ammonia and Juppo et al. [29] used 0.5 s as the pulse length of ammonia.

The thicknesses of the NbN_x thin films were determined with energy dispersive X-ray spectroscopy (EDX) using a Link ISIS EDX spectrometer installed to a Zeiss DSM scanning electron microscope (SEM). The EDX results were analyzed using a GMR Electron Probe Thin-Film Microanalysis program [32] and converted to physical thicknesses using the bulk density of NbN (8.4 g/cm) [7]. Film crystallinity was analyzed from the films deposited on glass substrates by a Philips MPD 1880 powder X-ray diffractometer (XRD) using the Cu Kα radiation. The composition of the films was determined by time-of-flight elastic recoil detection analysis (TOF-ERDA) [33,34] with 53 MeV $^{127}I^{10+}$ ions as the probing beam. Analysis of the TOF-ERD measurements was performed by using Monte Carlo Simulations [35] in order to reliably separate impurities in the NbN_x films from the surface and interface impurities (Fig. 1). The sheet resistance values were measured with a standard four-point probe method within 15 min after the films were exposed to air. The resistivity values were calculated using the thicknesses determined by the EDX analysis. The sheet resistance values of the samples storaged in air were remeasured after a few weeks but no significant changes were observed.